# BIODIESEL PRODUCTION FROM FRYER GREASE

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by

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# ABSTRACT

Biodiesel is a renewable, biodegradable, environmentally benign fuel for use in the diesel engines. It can be produced from renewable sources such as vegetable oils or animal fats. Although this fuel has gained worldwide recognition for many years, it is not being widely commercialized mainly because it is more expensive than petroleum diesel. A cheaper feedstock, such as fryer grease, may be used to improve the economics of biodiesel.

Methanol is the most common alcohol used in the transesterification process due to its low cost. However, recently, ethanol has been promoted as an alcohol for use in transesterification since it can be produced from renewable resources such as switchgrass, corn and wood, thereby reducing the dependency on petroleum sources (Pimentel and Patzek, 2005). A mixture of methanol and ethanol is hypothesized to take the advantages of both methanol and ethanol. The present work is focused on the production of biodiesel from fryer grease via transesterification with various mixtures of methanol and ethanol. Also, the kinetics of transesterification from fryer grease was studied.

Since fryer grease contains a high concentration of free fatty acids (FFA) (5.6 wt. %) and water (7.3 wt. %), a two-step acid/alkaline transesterification process was used to produce the esters. Sulfuric acid and potassium hydroxide were used as acid and alkaline catalysts, respectively. The methanol to ethanol molar ratio was varied from 3:3 to 5:1, whereas alcohol to oil molar ratio was maintained at 6:1. After the fryer grease was transesterified, all esters met ASTM standard D-6751. The viscosity of these esters ranged from 4.7 to 5.9 $mm^2/s$. The heating value of the esters was approximately 10%

less than that of petroleum diesel. The cloud point and pour point were in the range of 1 to -1 $^{o}$C and -3 to -6 $^{o}$C, respectively. When the mixed alcohol was used ethyl esters were also formed at a lower concentration along with methyl esters. The dominant fatty acid in fryer grease esters was found to be oleic acid. The lubricity of kerosene fuel was improved by as much as 33 % through the addition of these esters at rates as low as 1 %.

For the kinetic study of alkali-catalyzed transesterification of fryer grease, the alcohol to oil molar ratio, the reaction temperature, and the catalyst loading were varied as 6:1, 9:1, 12:1; 30, 40, 50 $^{o}$C; and 0.5, 1.0, 1.5 %, respectively. The ester concentration was found to rise with an increase in the catalyst loading or the reaction temperature and with a decrease in the alcohol to oil molar ratio. The overall forward and backward reaction orders were assumed to follow first and second order kinetics, respectively. The kinetic parameters were calculated using MATLAB. The conversion of triglyceride to diglyceride was found to be the rate determining step (RDS) of the overall reaction, with an activation energy of 36.9 kJ/mol.

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# DEDICATION

***This work is dedicated to***

***my family.***

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# ABBREVIATIONS

| | |
|---|---|
| AL | : Alcohol |
| AV | : Acid value |
| GC | : Gas chromatography |
| GC-MS | : Gas chromatography – Mass spectrometry |
| DG | : Diglyceride |
| E | : Activation energy |
| ES | : Ester |
| FFA | : Free fatty acid |
| FG | : Fryer grease |
| FEE | : Fryer grease ethyl ester |
| FME | : Fryer grease methyl ester |
| FMEE | : Fryer grease methyl ethyl ester |
| GL | : Glycerol |
| HPLC | : High performance liquid chromatography |
| HV | : Heating value |
| k | : Rate constant |
| LN | : Lubricity number |
| MG | : Monoglyceride |
| R | : Gas constant |
| RDS | : Rate determining step |
| T | : Temperature |
| TG | : Triglyceride |

# 1. INTRODUCTION

Growth in the world's population has resulted in a surge of energy demand. Conventional petroleum-based diesel fuel is not renewable and generates a significant amount of pollutants. Therefore, it is important to seek an alternative energy resource that is renewable and environmentally benign. Biodiesel is a promising source of energy. It is a renewable and biodegradable diesel fuel with less harmful emissions than petroleum-based diesel fuel. The recycling of $CO_2$ with biodiesel contributes to a 78% reduction of $CO_2$ emissions. Also, the presence of fuel oxygen allows biodiesel to burn more completely resulting in fewer unburned materials (U.S. Department of Energy, 2004). It can be used as pure form or blended with petroleum based diesel fuel. For example, lubricity of ultra low sulfur diesel fuel can be enhanced by 20% by adding 1 vol. % of canola-derived biodiesel (Lang et al., 2001b).

Biodiesel can be produced from vegetable oils or animal fats via a transesterification reaction. The major feedstock for biodiesel production in Canada is canola oil since Canada grows canola as its major oil crop. However, the cost of canola oil is somewhat high and hence the economics of biodiesel produced from canola oil could not compete with that of petroleum-based diesel fuel in North America. Therefore, a cheaper feedstock such as fryer grease is currently gaining interest from biodiesel producers. However, due to the presence of a number of impurities, a better technology is needed if a low quality feedstock is to be used to produce biodiesel.

Alkaline catalysts such as NaOH and KOH are the most commonly used in transesterification since their reaction is much faster than an acid-catalyzed reaction.

However, if high free fatty acid (FFA) feedstock such as fryer grease is used, the reaction is then partially driven to saponification which partially consumes catalysts and creates soap. Soap resulting from saponification creates difficulty in separating the by-product glycerol from biodiesel, which ultimately reduces the ester yield. Although acid-catalyzed transesterification does not encounter this problem, it requires a longer reaction time, higher reaction temperature, and a corrosion-tolerant reactor. The use of a two-step acid/alkaline catalyzed transesterification could be more suitable to produce biodiesel from high FFA feedstock such as fryer grease.

Alcohols used in transesterification are those of short chain carbon. The most popular one is methanol mainly because it is an economical source of alcohol. Also, the reaction can proceed faster if methanol is used due to its superior reactivity. However, solubility of oils in methanol is low, therefore transesterification is limited by mass transfer. Ethanol, on the other hand, possesses higher solubility and reduces the effect of the mass transfer limitation. In addition, ethanol can be produced from renewable resources such as switchgrass, corn**,** and wheat thereby reducing dependency from petroleum sources. The disadvantage of using ethanol involves the strong emulsion formed during transesterification which causes difficulty in the glycerol separation process. The mixture of methanol and ethanol are expected to perform better than either one due to the reasons mentioned above.

The current research work deals with the production of biodiesel from fryer grease using a two-stage acid/alkaline transesterification process with a mixture of methanol and ethanol. The objectives of this research work are (1) to produce ASTM grade biodiesel esters from fryer grease in a mixed methyl/ethyl system and

characterization of esters, and (2) to study the kinetics of alkali-catalyzed transesterification of fryer grease.

# 2. LITERATURE REVIEW

Biodiesel is a monoalkyl ester produced from renewable, biological resources for use in diesel engines. It is biodegradable and non-toxic, has low emission profiles, and therefore is environmentally beneficial (Ma and Hanna, 1999). In addition, it has excellent lubricity properties which reduce excessive engine wear caused by the use of ultra low sulfur diesel fuel (Lang et al., 2001b).

Biodiesel, can be used in its pure state or blended with petroleum-based diesel fuel. B20 is assigned for 20 vol. % biodiesel and 80 vol. % petroleum-based fuel blend. The substitution of pure biodiesel (B100) for petroleum diesel could reduce $CO_2$ accumulated in the atmosphere by 78 % due to $CO_2$ recycling by growing plants. In addition, other harmful substances such as particulate matter (PM), hydrocarbons (HC), and carbon monoxide (CO) are considerably reduced (U.S. Department of Energy, 2004).

## 2.1. Biodiesel from canola oil

In Canada, the major feedstock for biodiesel is canola oil, since canola is the largest oilseed crop. Canada grew 5.6 M hectares of canola in 1999-2000, with the majority being produced in Saskatchewan. Canada produces approximately 4,596,000 tonnes of canola annually and half of that is exported. Canola oil is an excellent feedstock for biodiesel production because oil content in canola seed ranges from 40 to 45 wt. % and it possesses good low temperature property (relatively low cloud point and pour point). This is because canola oil has a low saturated-fat level (having oleic acid as dominant fatty acid). Even though canola oilseeds are currently finding a market and not

all of them are available for feedstock for biodiesel production, there is still a large quantity available to make biodiesel (S&T Consultants Inc. and Meyers Norris Penny LLP, 2004).

Despite numerous advantages of biodiesel over petroleum based diesel, the local cost of biodiesel is higher than that of petroleum based diesel when fresh vegetable oils are used as feedstock as the Canadian oil price ranges from $0.4 to 1.0/kg. One of the solutions to this disadvantage is to employ a cheaper feedstock such as fryer grease, which will be discussed in section 2.3.

## 2.2. Biodiesel characteristics

In order to test the quality of biodiesel as a diesel fuel substitute, the American Society of Testing Materials (ASTM) has set a standard for biodiesel as a fuel for use in diesel engines. Numerous properties are included in the standard, such as kinematic viscosity, cetane number, flash point, sulfur content, water content, free glycerol, total glycerol, etc. (See Appendix A). It is important to control the quality of biodiesel to meet the ASTM standard before using it in a diesel engine. Problems with the use of biodiesel that does not meet the ASTM standard in a diesel engine are discussed below.

Appreciable amounts of sediment and water in biodiesel fuel tend to give trouble in fuel system of an engine. For example, an accumulation of sediment in storage tanks and on filter screens can obstruct the flow of oil from the tank. Water in fuels can cause corrosion of tanks and equipment, and if a detergent is present, the water can cause emulsions or a hazy appearance. Microbial growth can also occur if water is present.

Triglycerides and diglycerides, if present, would increase the overall viscosity of biodiesel ester and cause the formation of sediments when used in a diesel engine. The -OH group attached in free glycerol and monoglycerides are chemically aggressive toward non-ferrous metals and chromium-containing alloys, resulting in consequential damage on both the chrome-plated piston rings and sealing rings (Cvengroš and Cvengrošová, 2004). Hydroperoxides are very susceptible to an oxidation reaction yielding aldehydes and acids. In addition, hydroperoxides, if present, can induce polymerization and form insoluble gums and sediments. These compounds do not combust properly and result in carbon deposits (Ma and Hanna, 1999).

Distillation can be used to remove high molecular weight components such as mono-, di-, and triglycerides from the biodiesel ester. However, distillation at reduced pressure (vacuum) is required because the biodiesel will thermally decompose using atmospheric distillation. Since the fatty acid chains of the mono-alkyl esters, which comprise biodiesel, contain 16 to 18 carbons, they all have similar boiling temperatures, between 330 and 357°C. The specification value of distillation in the ASTM D6751 standard is set as 90% off at 360°C. This specification was incorporated to ensure that the fuel has not been adulterated with high boiling contaminants such as mono-, di-, and triglycerides.

The problem with the lubricity of petroleum-based fuel begins with the regulation to reduce sulphur content in diesel fuel to 15 ppm by 2006. In order for petroleum-based diesel to meet this low sulfur level limitation, desulfurization units have been introduced to refinery plants. However, during the process, polar heterocyclic nitrogen-containing compounds which contribute to the lubricating property of the fuel are also removed

along with sulfur (Barbour et al., 2000). When used in a diesel engine, the desulfurized diesel fuel causes premature engine wear and malfunction. To restore the lubricity of diesel fuel, refiners regularly add various lubricity additives in the diesel fuels. Fatty acid esters can act as a lubricity additive for diesel fuel.

Free fatty acids in a biodiesel may increase the likelihood of corrosion. The unsaturated free fatty acids are susceptible to an oxidation reaction, which leads to the formation of hydroperoxides and ultimately increases deposits in fueling system.

A biodiesel ester is subjected to oxidation through contact with oxygen in the air. The extent of the level of oxidation can be determined by the peroxide value. Most vegetable oils contain natural anti-oxidant reagents, i.e. Vitamin E (tocopherol), which hinder the oxidation reaction. Once the amount of anti-oxidants is depleted, the rate of oxidation grows up rapidly. The period from the starting point to the point where fast oxidation begins is known as the "induction period". It is reported that the peroxide value increases proportionally to the number of double bonds in the ester. For instance, linoleic acid (which contains two double bonds) oxidizes faster than oleic acid (which contains one double bond). In order to minimize the total glycerol content (one of the ASTM requirements) in biodiesel, distillation can be used to remove high boiling point materials such as acylglycerols. However, Gerpen (1996) has shown that the distilled biodiesel has a higher peroxide value than the undistilled one and is more prone to oxidation. He explained that during the distillation process, natural anti-oxidants such as Vitamin E are also removed which leads to the higher peroxide value and hence, reduced stability.

## 2.3. Availability and properties of fryer grease

As mentioned in section 2.1, the major disadvantage of biodiesel is its higher cost compared with petroleum diesel fuel. The cost of petroleum based diesel is approximately 0.35 US$/kg while cost of biodiesel (B100) is approximately 0.67 US$/kg (S&T Consultants Inc. and Meyers Norris Penny LLP, 2004). Zhang et al. (2003) reported that on average a $0.01/kg increase in canola seed cost would result in $0.03/kg increment in biodiesel price. It was also reported that raw material cost is responsible for approximately 70-95 % of biodiesel production cost when fresh vegetable oil is used as feedstock. Therefore, the use of fryer grease (FG), which is much cheaper than fresh vegetable oils, should greatly assist in improving the economics of biodiesel (Canakci and Gerpen, 2001).

The frying process, defined as the process where the fat is heated in the presence of air at temperatures ranging from 160 to $200^0$C, has been popular for food preparation throughout history (Cvengroš and Cvengrošová, 2004). Fryer grease is usually generated by the frying process. Fryer grease usually contains various compounds such as di- and monoglycerides, free fatty acids (FFA), aldehydes, etc, in addition to triglycerides (the main component in fresh vegetable oil). There are a number of studies attempting to find out what exactly happens during the frying process as the chemistry of frying oils is still not fully understood. The main reactions involved in the frying process are thermolytic, hydrolytic, and oxidative (Nawar, 1984). One possible reaction is depicted in Figure 2.1. Nawar (1984) explained that the initiation step involves the production of free radicals (R·). The reaction is propagated by the abstraction of hydrogen atoms to the double bonds

Initiation:

$$RH \rightarrow R^{\bullet} + H^{+}$$

Propagation:

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet}$$

$$ROO^{\bullet} + H^{+} \rightarrow ROOH$$

$$ROOH \rightarrow RO^{\bullet} + OH^{\bullet}$$

Termination:

$$RO^{\bullet} + H^{+} \rightarrow ROH$$

$$OH^{\bullet} + H^{+} \rightarrow H_2O$$

Figure 2.1: Scheme for the free radical autoxidation mechanism.

in unsaturated molecules. Then, oxygen drawn from the air attacks at these locations to form peroxide radicals (ROO·), which further give rise to hydroperoxides (ROOH). These hydroperoxides tend to proceed toward oxidative degradation and lead to secondary oxidation products. As the frying process proceeds, fryer grease develops many polymerized materials and unknown toxic compounds which are harmful to human health and hence cannot be used for edible purposes.

There are two types of grease: yellow grease (FFA < 20 wt. %) and brown grease (FFA > 20 wt. %). The price of yellow grease is significantly lower than that of fresh vegetable oils. The dumping fee for brown grease can vary depending on its quality. Feedstock costs for biodiesel production are presented in Table 2.1.

The availability of fryer grease as a feedstock for biodiesel production is highly related to area population. Yellow grease generated in Canada is roughly equivalent to 4 kg production per person per year. Therefore, there would be approximately 124 kilotonnes of yellow grease produced in Canada (S&T Consultants Inc. and Meyers Norris Penny LLP, 2004). Although feedstock to produce biodiesel can not depend totally on fryer grease, a significant amount of biodiesel can be produced from it.

## 2.4. Transesterification of vegetable oil

Transesterification is the reaction of fats or oils with alcohols to form biodiesel esters and glycerol. Figure 2.2 shows the overall scheme for transesterification of triglycerides. A catalyst is required to improve the reaction rate and yield.

Alkaline and acidic catalysts are commonly used for biodiesel production. The alkali-catalyzed reaction is reported to be much faster than the acid catalyzed one

Table 2.1. Feedstock prices for biodiesel production (Tyson, 2002)

| Feedstock | Price [¢/lb] |
|---|---|
| Sunflower | 20 |
| Corn | 19 |
| Soy | 18 |
| Yellow grease | 9 |
| Brown grease | -5 to 5 |

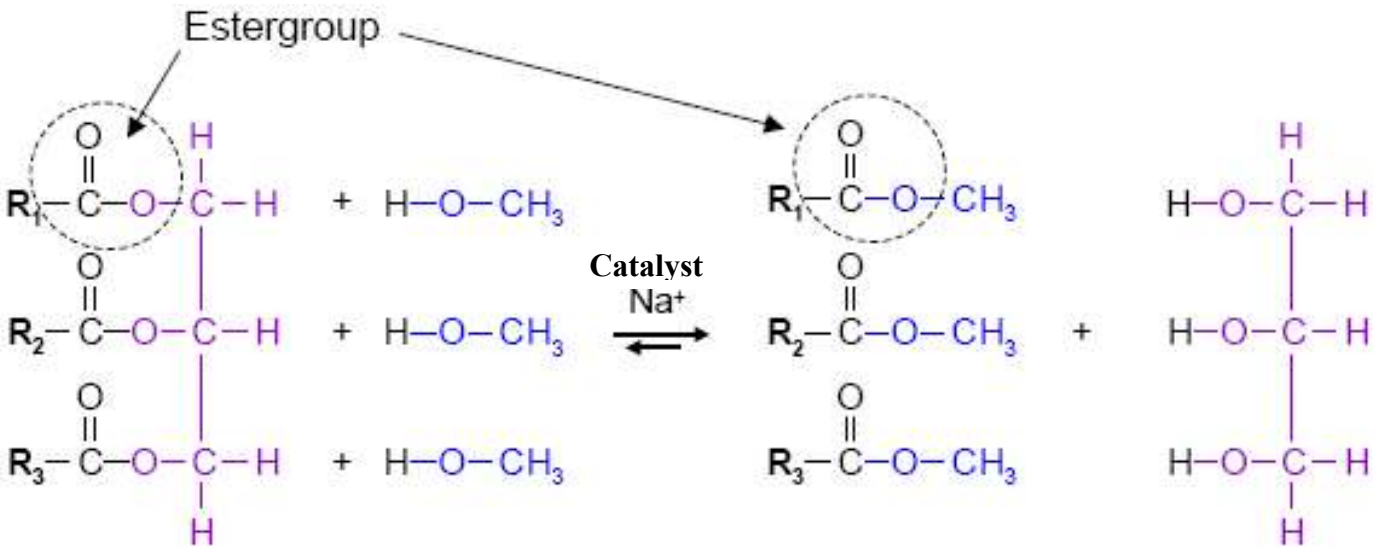
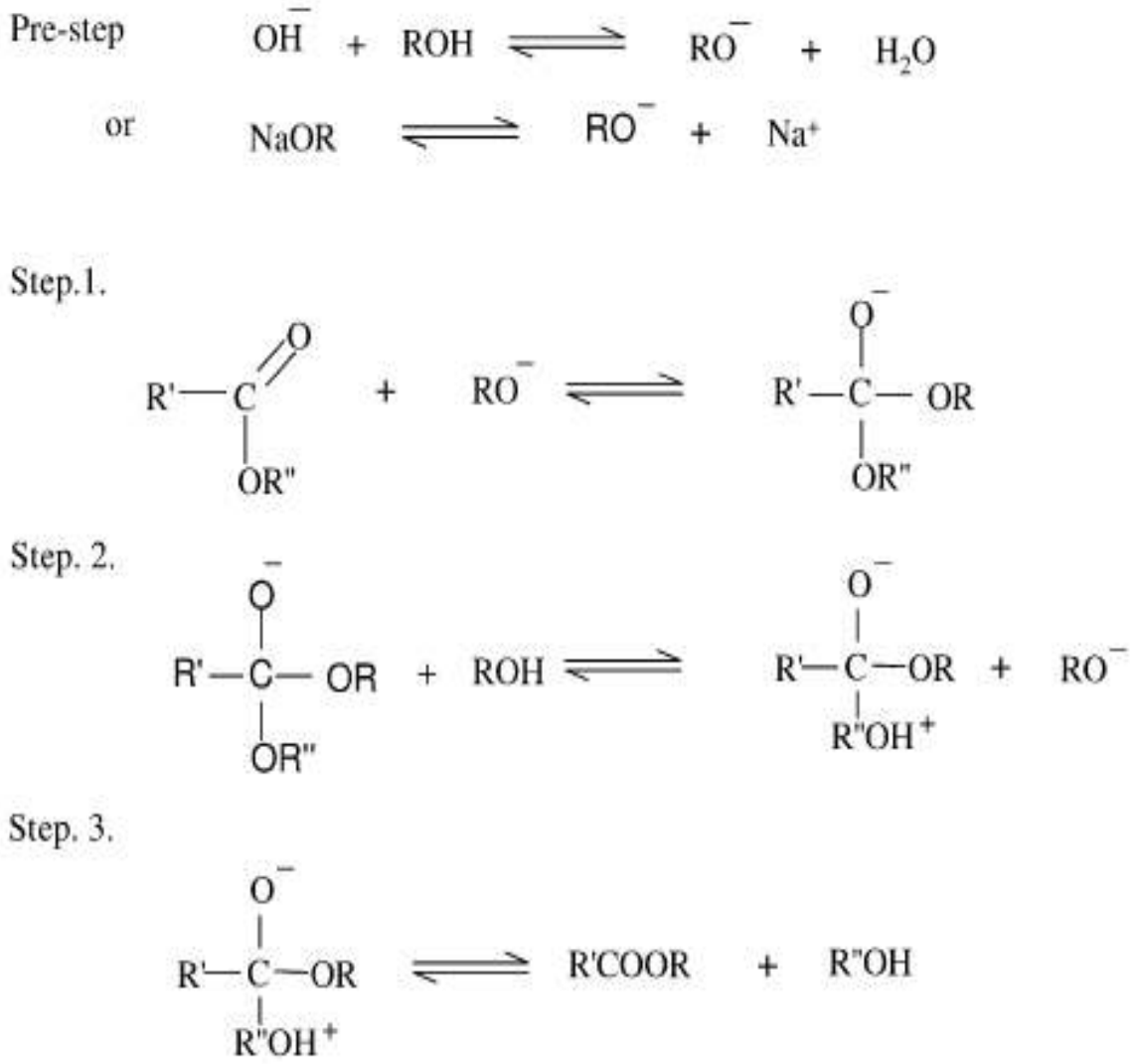



Figure 2.2: Overall scheme of the triglyceride transesterification.

(Freedman et al., 1984). The examples of alkaline catalyst are sodium hydroxide (NaOH), potassium hydroxide (KOH), and corresponding sodium and potassium alkoxides such as sodium methoxide ($NaOCH_3$) and sodium ethoxide ($NaOC_2H_5$). Lang et al. (2001) reported the equal effectiveness of both KOH and $NaOCH_3$ as alkaline catalysts for transesterification of canola oil with methanol. However, KOH is more economical than $NaOCH_3$, thus making it the more popular catalyst for the transesterification of vegetable oil. An alkaline catalyst is not a proper choice for transesterification containing high FFA feedstock. This is because FFA would drive the reaction partially to saponification which consumes the catalyst, lowers ester yield, and causes difficulty in glycerol separation. Water, if present, would also favour saponification. Acid catalysts can also be used for transesterification. The examples of acid catalysts are sulfuric acid ($H_2SO_4$), sulfonic acids ($RSO_3H$), and hydrochloric acid (HCl). Acid catalysts are insensitive to FFA. However, there are a number of serious problems associated with acid catalyzed reactions such as slow reaction rate, requirement of high operating temperature and high alcohol to oil molar ratio, and the requirement of an anti-corrosion reactor. Mechanisms of alkali- and acid catalyzed transesterification are shown in Figure 2.3 and 2.4, respectively.

In the case of feedstock with FFA up to 20%, the two step acid-alkaline catalyzed transesterification process can be used to produce biodiesel. This process starts with acid-catalyzed esterification of FFA followed by alkali-catalyzed transesterification of acylglycerol. Feedstock with lower FFA content (FFA < 4 wt. %) can be purified either by separation of FFA or saponification of FFA with alkaline (also known as caustic stripping) then transesterifying triglycerides using an alkaline catalyst. Alternatively, FFA

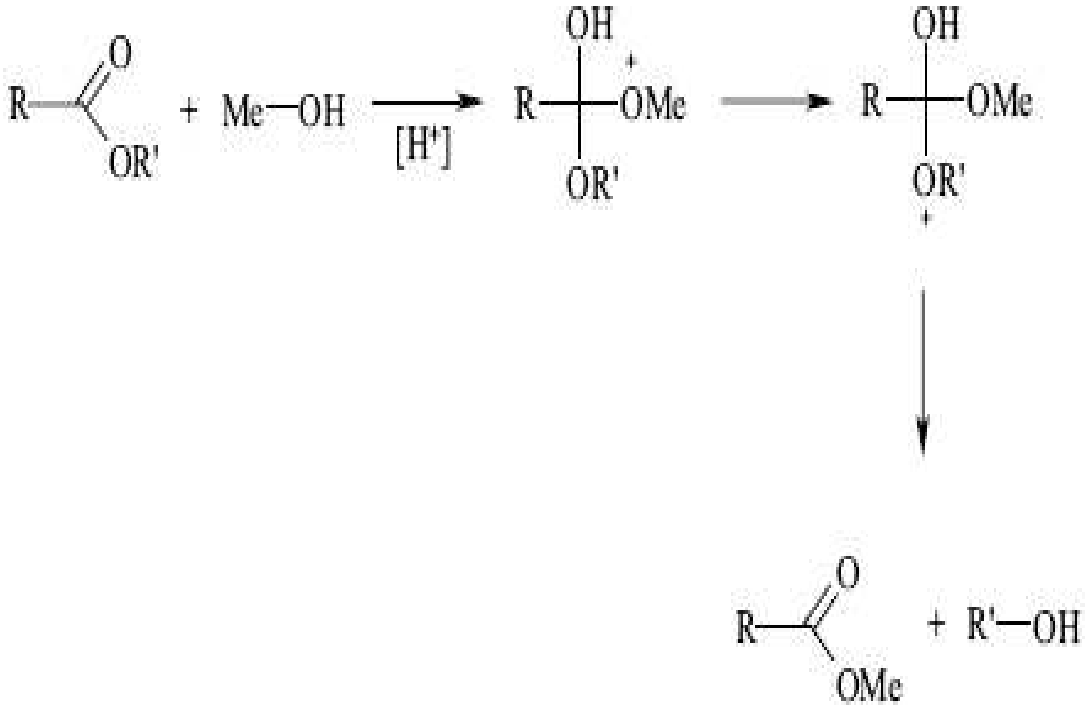



where R = short alkyl group

R' = long chain alkyl group

R" = glycerol backbone attached to fatty acids or without fatty acids

Figure 2.3: Mechanism of alkali-catalyzed transesterification (Ma and Hanna, 1999).




where Me = $CH_3$

R = long chain alkyl group

R' = glycerol backbone attached to fatty acids or without fatty acids

Figure 2.4: Mechanism of acid-catalyzed transesterification (Lifka and Ondruschka, 2004).

can be turned into acylglycerol followed by transesterification of acylglycerol to produce esters (Tyson, 2002).

Since transesterification is known to be a reversible reaction, excess alcohol is required in order to shift the equilibrium to the product side (Ma and Hanna, 1999). Alcohols used in transesterification are usually short-chain alcohols such as methyl, ethyl, propyl, and butyl alcohol. Methanol is the most popular alcohol being used in the transesterification process because of its relatively cheaper price compared to other alcohols. Ethanol on the other hand, can be produced from renewable resources thereby reducing dependency on the petroleum resource. The kinetics of transesterification using different alcohols will be discussed in section 2.6.

To obtain high biodiesel yield, the substantially anhydrous feedstock with FFA less than 0.5 % is required for alkali-catalyzed transesterification (Freedman et al., 1984). The recommended condition for transesterification of vegetable oils with methanol is with an alcohol to oil molar ratio 6:1, 1 %KOH at 25$^{o}$C, for 30 min. (Tomasevic and Siler-Marinkovic, 2003).

After transesterification, the product consists of esters, glycerol, catalyst, unreacted alcohol, tri-, di-, and monoglycerol. Product ester needs to be purified since the contaminated compounds could cause degradation of the produced biodiesel. The adverse effects of the contaminated acylglycerol and glycerol were described in section 2.2. The blends of purified esters and petroleum based diesel fuel have proven to perform more efficiently than the pure petroleum based diesel fuel in diesel engines and to generate less engine emissions (Al-Widyan et al., 2002).

## 2.5. Glycerol utilization

One of the significant factors affecting biodiesel price is the value of the by-product glycerol. It was reported that a $0.11/kg increase in glycerol price could cause a decrease in biodiesel price by $0.01/kg (Zhang et al., 2003). Glycerol can be refined into glycerine, a clear, odourless, gel-like substance, which is used in many industrial sectors such as food and beverage, pulp and paper, pharmaceutical, textile, and cosmetic. Moreover, glycerol value can be improved if novel ways of glycerol utilization are developed. Recently, there are a number of studies focused on glycerol utilization such as $H_2$ production and value added liquid chemicals production including aldehydes and ketones (Chaudhari and Bakshi, 2002, Buhler et al., 2002).

The federal Climate Change Action Plan calls for the annual production of 500 million litres of biodiesel in Canada by 2010 (Smith, 2004). This would result in an annual production of approximately 50 million litres of glycerol. With such large amounts of glycerol being produced as a by-product of transesterification process, its utilization is of significant importance and would partly improve the economics of biodiesel.

## 2.6. Kinetics of transesterification

Kinetic data is of great importance in terms of process assessment and development. Transesterification consists of a series of consecutive, reversible reactions where triglyceride gives rise to diglyceride, diglyceride gives rise to monoglyceride, and finally monoglyceride gives rise to glycerol as shown in Figure 2.5. In each step, one mole of ester is formed per one mole of acylglycerol consumed.

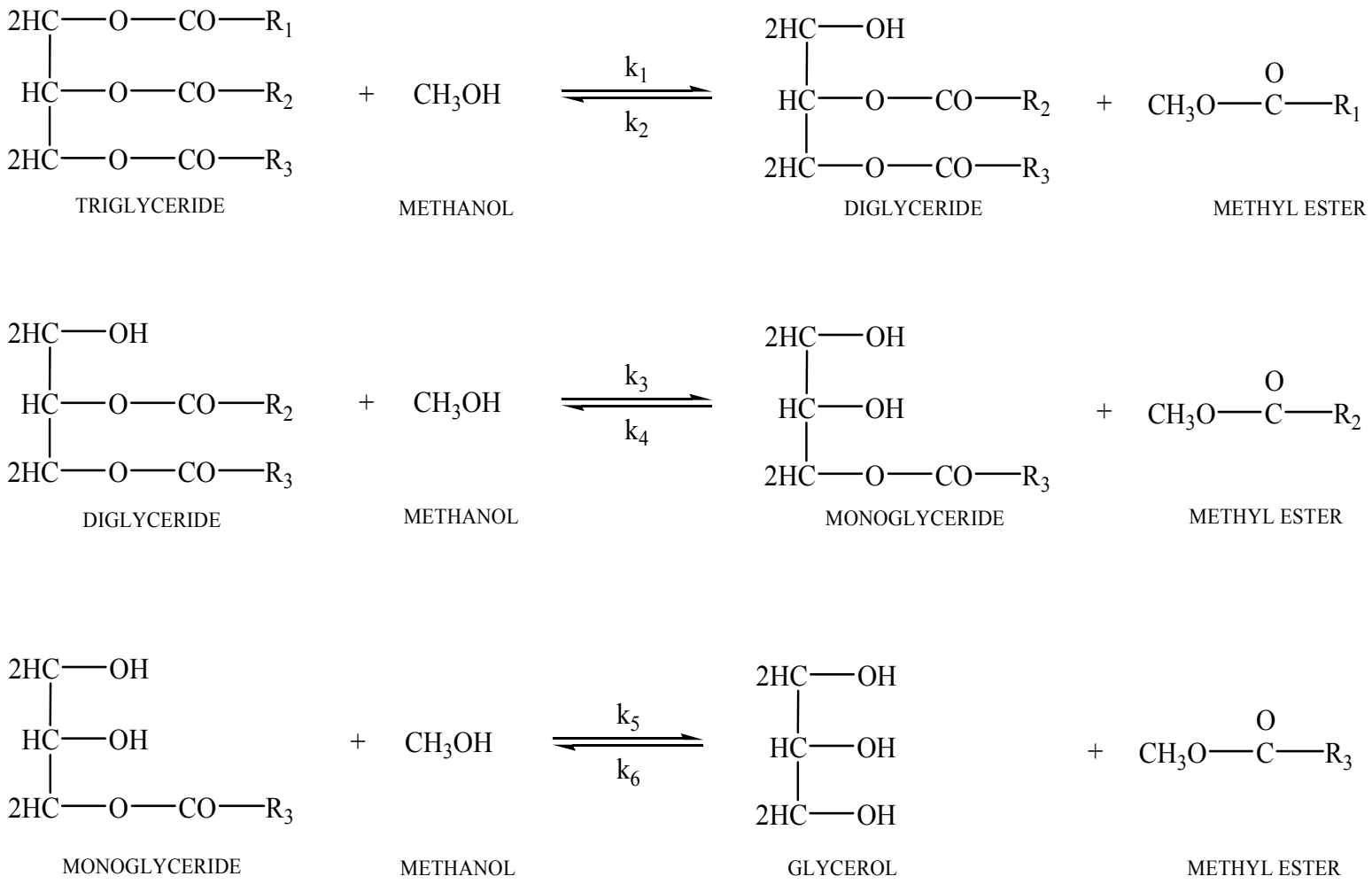



Figure 2.5: Triglyceride transesterification reaction scheme.

Methanol and ethanol are not miscible with oil at room temperature, hence the reaction mixture is usually mechanically stirred to improve rate of mass transfer. At the initial stage of the reaction, acylglycerol in the oil phase takes a significant amount of time to dissolve into the alcohol phase where the catalyst resides. The amount of time necessary for this process depends highly on the solubility of oil in alcohol and hence, the type of alcohol has a great effect on how fast the reaction can occur. Oil is more soluble in ethanol than methanol. The larger nonpolar group in ethanol is assumed to be a crucial factor for the better solubility in ethanol. However, for the same reason, the emulsion formed during ethanolysis is stronger and more difficult to break down than that formed during methanolysis. The unreacted di- and monoglycerides possess both polar and nonpolar groups and are assumed to be a crucial compound stabilizing the emulsions (Zhou et al., 2003). Therefore, the completion of the reaction is essential for the good separation of glycerol from biodiesel. It is more likely for the equilibrium of methanolysis to be closer to completion in comparison to those when other alcohols are used. This is because the methoxide ion, the actual catalyst, formed as a result of ionization of methanol, is most reactive among those ions formed from other alcohols, i.e., ethanol, propanol, and butanol. The relative reactivity of methyl, ethyl, *n*-propyl, and *n*-butyl group is 1.00, 0.81, 0.79, and 0.80, respectively (Sridharan and Mathai, 1974). The mixture of methyl-ethyl alcohol is hypothesized to take advantage of good solubility from ethanol and good glycerol-biodiesel separation and reaction equilibrium from methanol. In addition, if part of the methanol is replaced by ethanol, there would be less dependency on the synthetic sources of methanol.

There are a number of published research papers related to the kinetic study of transesterification of vegetable oils. Freedman et al. (1984) studied the kinetics of transesterification of cottonseed, peanut, sunflower, and soybean oil with methanol and butanol. Various alcohol to oil molar ratios were used with $NaOCH_3$, NaOH and $NaOC_4H_9$ as alkaline catalysts and $H_2SO_4$ as an acid catalyst. A plot of ester percentage vs. time showing an S-shape curve during transesterification was obtained as shown in Figure 2.6. This indicates that the rate of ester formation was slow initially as well as prior to completion. In the case of 3:1 alcohol to oil molar ratio, a lower percentage of ester was obtained as compared to the case when a 6:1 alcohol to oil molar ratio was used. Optimum alcohol to oil molar ratio is suggested as 6:1. The further increase in alcohol to oil molar ratio would not help to improve ester yield but only add cost to alcohol recovery. At 6:1 alcohol to oil molar ratio, 0.5% $NaOCH_3$ was as effective as a 1.0% NaOH catalyst. In conclusion, it is recommended that a substantially anhydrous feedstock for transesterification with FFA content less than 0.5% is required. The optimum conditions recommended are a 6:1 alcohol to oil molar ratio with either 0.5% sodium methoxide or 1.0% sodium hydroxide as a catalyst.

Freedman et al. (1986) investigated the kinetics of methanolysis and butanolysis of soybean oil. The catalysts used were $NaOCH_3$ and $NaOC_4H_9$ as alkaline catalysts and $H_2SO_4$ as an acid catalyst. The reaction was much slower under acidic conditions than those when an alkaline catalyst was used. It was reported that the forward reactions followed pseudo-first-order kinetics while backward reactions followed second-order kinetics. In the alkali-catalyzed reaction, the reaction of NaOBu-catalyzed butanolysis

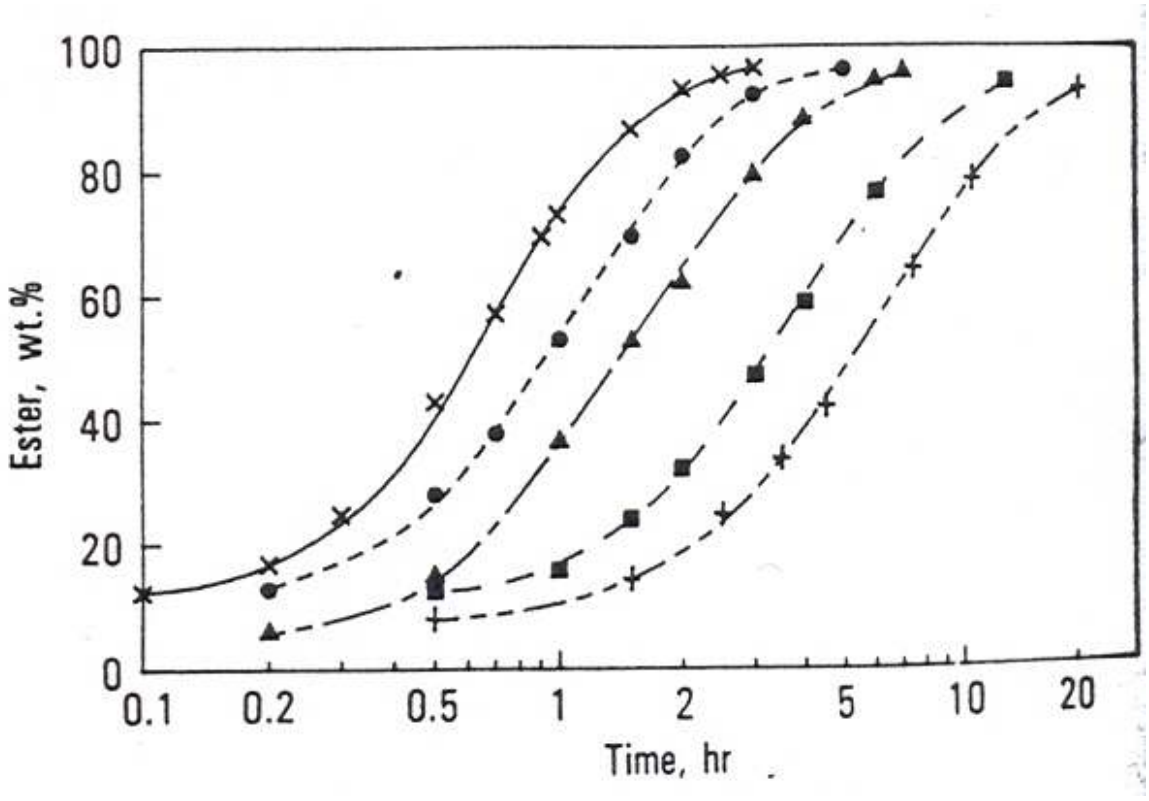



Figure 2.6: Experimental results from Freedman et al. (1986) showing ester formation from soybean oil transesterification. ×, 117 °C; ●, 107 °C; ▲, 97 °C; ■, 87 °C; +, 77 °C.

was reported to follow second order kinetics while the reaction of $NaOCH_3$-catalyzed methanolysis was somewhat deviated from second order kinetics. In the case of methanolysis, a rapid increase of methyl ester was observed without a rapid change in di- and monoglyceride. Therefore, they have proposed a shunt reaction in which all three chains of the triglyceride molecule were simultaneously attacked by methanol or, more accurately, by methoxide ions.

Boocock et al. (1995) disagreed with the "shunt reaction" mechanism proposed by Freedmen et al. (1986). They argued that there is no sound reason why three methoxide ions would simultaneously attack a triglyceride molecule. Alternatively, they explained this phenomenon in terms of the limitation of mass transfer due to the nature of the two phase system. Since oil is not miscible with methanol, it takes significant time for oil to dissolve in methanol. The reaction is therefore limited by the oil concentration in the methanol phase where the catalyst locates. The hydroxyl group in mono- and diglycerides makes them more soluble in methanol than for the triglyceride. Once dissolved in the methanol phase, there is more chance for mono- and diglyceride to react with methanol than to transfer back to the oil phase. This explains Freedman's result; where no rapid change of the intermediate mono- and diglycerides was observed. To overcome this mass transfer limitation due to the two phase reaction, tetrahydrofuran (THF) was used as a co-solvent to render a single phase of oil-methanol. The rate of reaction increased significantly after THF was added into the system.

Boocock and co-workers (Boocock et al., 1998) introduced the concept of catalyst depletion and polarlity of the reaction mixture to explain the behaviour of ester formation in which the rate of ester formation becomes decelerated at the final stage of the reaction.

They measured the percentage of depletion of hydroxide ion concentration during methanolysis of soybean oil and compared it with the rate of ester formation. They concluded that the half life of the hydroxide catalyst is too long to explain the deceleration of ester formation. Then they compared transesterification of soybean oil with coconut oil. The coconut oil has a shorter alkyl group than that in the soybean oil hence making it more polar than soybean oil. They observed that methanolysis of coconut oil occurred faster than that of soybean oil. Their result indicates that polarlity does play a role in the reaction.

Sunflower oil was transesterified with ethanol using KOH as a catalyst (Zhou et al., 2003). The alcohol to oil molar ratio, reaction temperature, and catalyst concentration were varied in the range of 6:1 to 30:1, 23 $^{o}$C to 60 $^{o}$C, and 0.5 wt.% to 1.4 wt.% respectively. They found that increasing the alcohol to oil molar ratio, the reaction temperature, and the catalyst concentration can cause equilibrium of the reaction to be achieved earlier.

Vicente et al. (2005) studied the kinetics of sunflower oil methanolysis using various impeller speeds. They found that at an impeller speed of 600 rpm, the region of mass transfer at the initial stage of the reaction can be determined insignificant. The rate constant corresponding to conversion of glyceride to monoglyceride was comparatively low, therefore such a reaction was not favored. The cause is the immiscibility of the ester and glycerol. The reaction rates were found to increase linearly with catalyst concentration and the effects of catalyst concentration were especially significant for the second forward and reward step (diglyceride $\leftrightarrow$ monoglyceride). Reaction at all temperatures was very rapid and the effect of temperature on reaction rates was trivial.

However, the reaction rate was lower at the lowest temperature (25 $^{o}$C) in the initial stage of the reaction.

# 3. EXPERIMENTAL PROCEDURES FOR BIODIESEL PRODUCTION

## 3.1. Materials

Fryer grease was procured from "Saskatoon Processing Company", Saskatoon, Canada. Anhydrous methanol (MeOH), 99.8%, and anhydrous ethanol (EtOH) were purchased from EMD Chemicals Inc., Darmstadt, Germany and Commercial Alcohol Inc., Brampton, ON, Canada, respectively. Potassium hydroxide (KOH) purchased from EMD Chemicals, Darmstadt, Germany and sulfuric acid ($H_2SO_4$) from EM Science, Darmstadt, Germany were used as catalysts in alkali and acid catalyzed reactions, respectively. Hydrochloric acid (HCl), 37-38% pure, and potassium iodide (KI) were obtained from EMD Chemicals Inc., New Jersey, USA. Carbon tetrachloride ($CCl_4$) and potassium dichromate ($K_2Cr_2O_7$) were purchased from BDH Chemicals, Toronto, Canada. Sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$), and Wijs solution (which contains iodine monochloride and acetic acid) were purchased from Fisher Scientific Company, New Jersey, USA, and VWR International, USA, respectively. Silica gel (28-200 Mesh) from EMD chemicals, New Jersey, USA with adsorption capacity of 22 kg $H_2O$/100 kg was used for removing moisture from biodiesel.

## 3.2. Production and characterization of biodiesel from fryer grease

### *3.2.1. Pre-treatment of fryer grease (FG)*

The FG obtained from Saskatoon Processing Company is a mixture consisting of tri-, di-, monoglyceride, water, solid particles, free fatty acids (FFA) and many other

chemicals. Properties of crude FG are shown in Table 3.1. Since water and FFA create problems during the transesterification, FG was pre-treated before the reaction. The solid portion of FG was removed using the centrifuge universal 32 R supplied from Hettich Zentrifugen, Germany. Water was removed by mixing FG with 10 wt% silica gel followed by stirring the mixture and vacuum filtration. This step was conducted twice to ensure complete removal of water. Water content of crude FG and silica gel treated FG was evaluated using a Karl Fisher Titrator, (ATI ORION, 950 Ross).

*3.2.2. Transesterification of fryer grease using an alkaline catalyst*

Transesterification of FG using an alkaline catalyst was carried out with a two-step process. The two-step reaction utilized a 100% excess methanol, 6:1 molar ratio of alcohol to oil and 1% KOH as a catalyst. In each step, 3 moles of alcohol and 0.5% KOH were used and the reaction was carried out at 25$^{o}$C for 30 min. After the first step, the FG having high free fatty acids formed thick soap which interfered with the glycerol separation. No further experiment was done with this method because of the saponification reaction.

*3.2.3. Production of biodiesel using the two-step acid/alkali-catalyzed method*

In order to avoid the problem of saponification, a two-step method was used for synthesis of biodiesel from FG. The flow chart of the two-step acid/alkali-catalyzed transesterification process is as shown in Figure 3.1. In the first step, esterification of FFA present in FG was carried out using sulphuric acid as a catalyst and in the second step, transesterification of the neutral FG was performed using KOH as a catalyst. Esterification of FFA was carried out as follows: A 50 g of FG was placed in a batch reactor equipped with glass stopper, thermometer, and a magnetic stirrer. In another

Table 3.1. Properties of crude fryer grease

| Property | Value | Method |
|---|---|---|
| Solids | 19 % | -- |
| Total polar compounds | 22 % | AOCS Cd 20-91 |
| Polymerized triglycerides | 1.43 % | IUPAC, 2.508 (1987) |
| Oxidized triglycerides | 4.72 % | IUPAC, 2.508 (1987) |
| Acid value | 11.2 $mgKOH \cdot g^{-1}$ | AOCS Te 1a-64 |
| Free fatty acid (FFA) | 5.6 % | -- |
| Water content | 7.3 % | Karl Fischer method |
| Saponification value | 177.87 $mgKOH \cdot g^{-1}$ | AOCS Cd 3-25 |
| Iodine value | 94.5 cg $Iodine \cdot g^{-1}$ | AOCS Tg 1-64 |

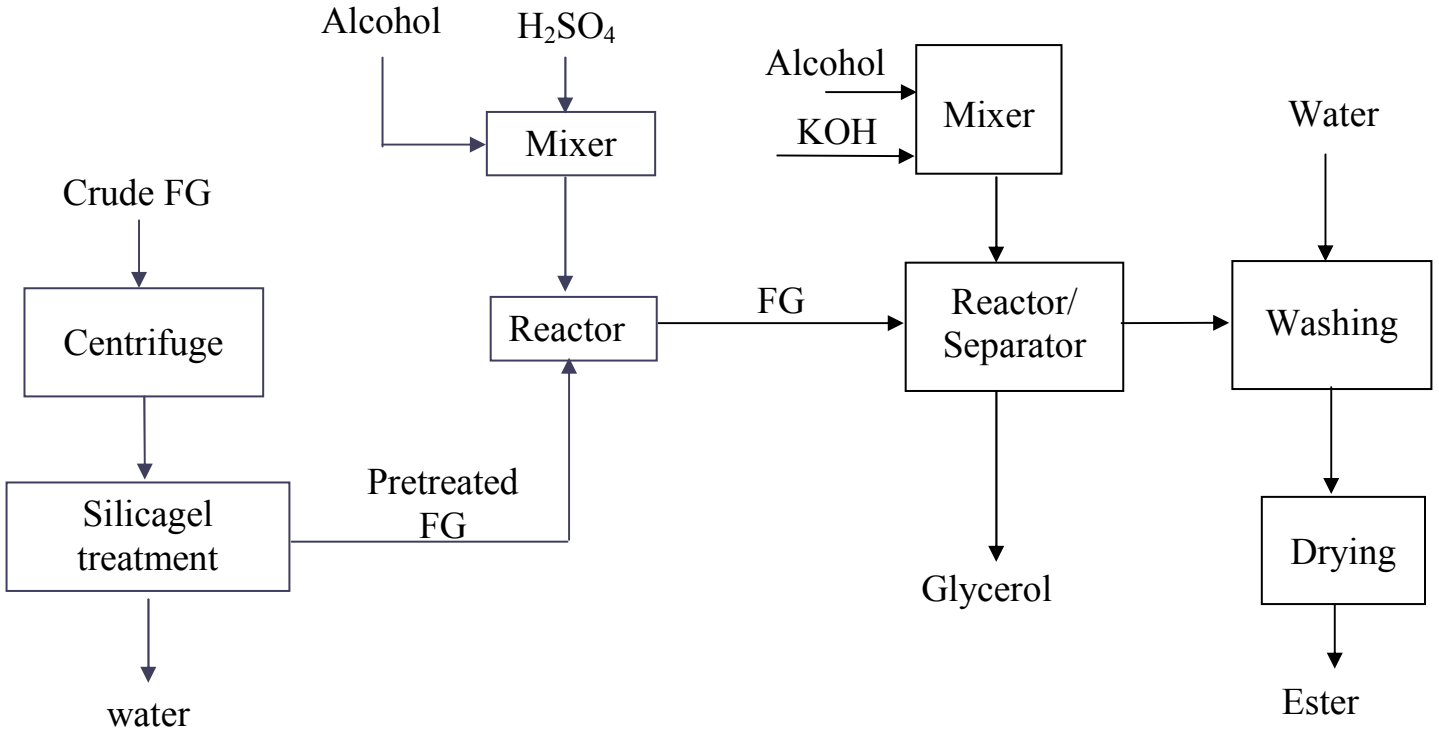



Figure 3.1: Scheme for the two-step acid/alkali-catalyzed transesterification of fryer grease.

flask, 2 wt% of sulphuric acid with respect to the FG was mixed with alcohol (3:1 alcohol to FG ratio) for esterification of FFA in FG (See Appendix B for sample calculations) and then poured to the FG. To avoid the evaporation of alcohols, the reaction temperature of 50$^{o}$C was selected for methanol and the mixture of alcohols, and 60$^{o}$C for ethanol. Depending on the decrease in acid value of FG, the esterification reaction was continued for up to 5 hrs. Transesterification of the esterified FG was carried out using KOH as a catalyst. Next, 0.5 g (1 wt. % with respect to FG) plus 1.144 g (to neutralize the $H_2SO_4$) of KOH was properly mixed in alcohol and poured into the reaction mixture for transesterification (See Appendix B), which was carried out for one hr at 25, 50, and 60$^{o}$C using methanol, the mixture of alcohols, and ethanol, respectively.

*3.2.4. Purification of esters*

After transesterification the co-product glycerol was separated by gravity in a separating funnel. In the case of fryer grease used in ethyl ester production, the glycerol could not be separated by gravity. To separate the glycerol from ester phase, 2 g of pure glycerol was added to the reaction mixture and stirred for 15 min at 25 $^{o}$C. To ensure complete glycerol separation, this step was repeated 2-3 times. The methyl ester phase was then washed with hot distilled water at ~90 $^{o}$C to remove the catalyst. In the case of mixed esters and ethyl ester, the washing was done in a similar manner as with methyl ester except that 0.1 wt% tannic acid solution in distilled water was used (instead of pure distilled water) in order to avoid the emulsion. Unreacted alcohol and water were removed by vacuum distillation at ~90$^{o}$C for 1.5 hrs using a BÜCHI Rotavap R-114 equipped with BÜCHI Waterbath B-480, purchased from BÜCHI Labortechik AG, Switzerland.

*3.2.5. Characterization of Esters*

The biodiesel esters were characterized for their physical and chemical properties. Standard methods applied for ester characterization are presented in Table 3.2. The details on equipment and procedures are presented as follows:

*3.2.5.1. Physical characterization*

The esters were extensively characterized for their physical properties such as viscosity, heating value, cloud point, pour point, boiling point distribution, and lubricity property.

The viscosity of esters was measured at 40 $^{o}$C using a Brookfield Digital viscometer Model DV-II. The temperature bath was turned "on" and sufficient time was allowed for the sample cup to reach 40 $^{o}$C. The sample cup was then removed and the spindle CP-40 was carefully attached to the lower shaft. Then, 0.5 ml of sample was spread evenly over the surface of the sample cup. Again, sufficient time was allowed for the sample fluid to reach 40 $^{o}$C. The motor switch was turned "on" and sufficient time was allowed for the display reading to stabilize.

Heating value is another important property of an ester as it is aimed for use as a diesel fuel substitute. An oxygen bomb calorimeter series 1300 (Parr Instrument Company, Illinois, USA) was used to measure the heating values of esters. A 1 ml of the sample was weighed and put in the metal combustion capsule. The capsule was then placed on the sample holder where 10-cm of fuse wire was attached. Then 1 ml of distilled water was placed in the bomb and the head of the bomb (attached with sample holder) was fixed on the bomb. The bomb was sealed by closing the screw

Table 3.2. Standard methods for ester characterization

| **Property of esters** | **Test method** |
|---|---|
| Fatty acid compositions | AOCS method Ca 5a-40 |
| Acid value | AOCS method Te 1a-64 |
| Heating value | ASTM D240-92 |
| Cloud point | ASTM D2500 |
| Pour point | ASTM D97 |
| Iodine number | AOCS method Tg 1-64 |

cap on top of the head firmly. The oxygen was then filled in the bomb with a pressure of approximately 25 atmospheres. The calorimeter bucket containing 2000 g of distilled water was placed inside the calorimeter jacket. Then the bomb was lowered in the water inside the bucket. Sufficient time was allowed to observe the bomb to ensure the complete absence of any oxygen leakage from the bomb. The two ignition lead wires were then placed in the terminal sockets on the bomb head and the jacket was set with the cover. The motor was turned "on" to run the stirrer. The first 5 min. was dedicated to the system reaching equilibrium. The initial temperature was recorded at the $6^{th}$ min. The ignition button was pushed to ignite the fuel in the bomb. There was an increase in temperature until it reached maximum point. The final temperature was then recorded. Then the bomb was removed from the bucket and all interior surfaces were washed with 5 ml of distilled water. The washing water was collected in a beaker and titrated with 1.0 N $Na_2CO_3$. The unburned pieces of fuse wire were collected from the bomb electrodes and were measured to determine the net amount of wire burned. The equation used to calculate heating value is shown below:

$$HV = \frac{(\Delta T \times 2470) - V - L - 2.3}{W} \times \frac{4.184}{1000} \quad \text{... (3.1)}$$

where HV = heating value [MJ/kg]; $\Delta$T = difference between initial temperature and final temperature [$^{o}$C]; V = titration volume [ml]; L = length of wire burned [cm]; W = weight of liquid sample [g].

Cloud point is the temperature at which a cloud of wax crystals first appears in the oil when it is cooled. Pour point is the lowest temperature at which the oil specimen can still be moved. Cloud point and pour point are used to measure the cold temperature usability of an ester as a fuel. Cloud and pour points were determined simultaneously as

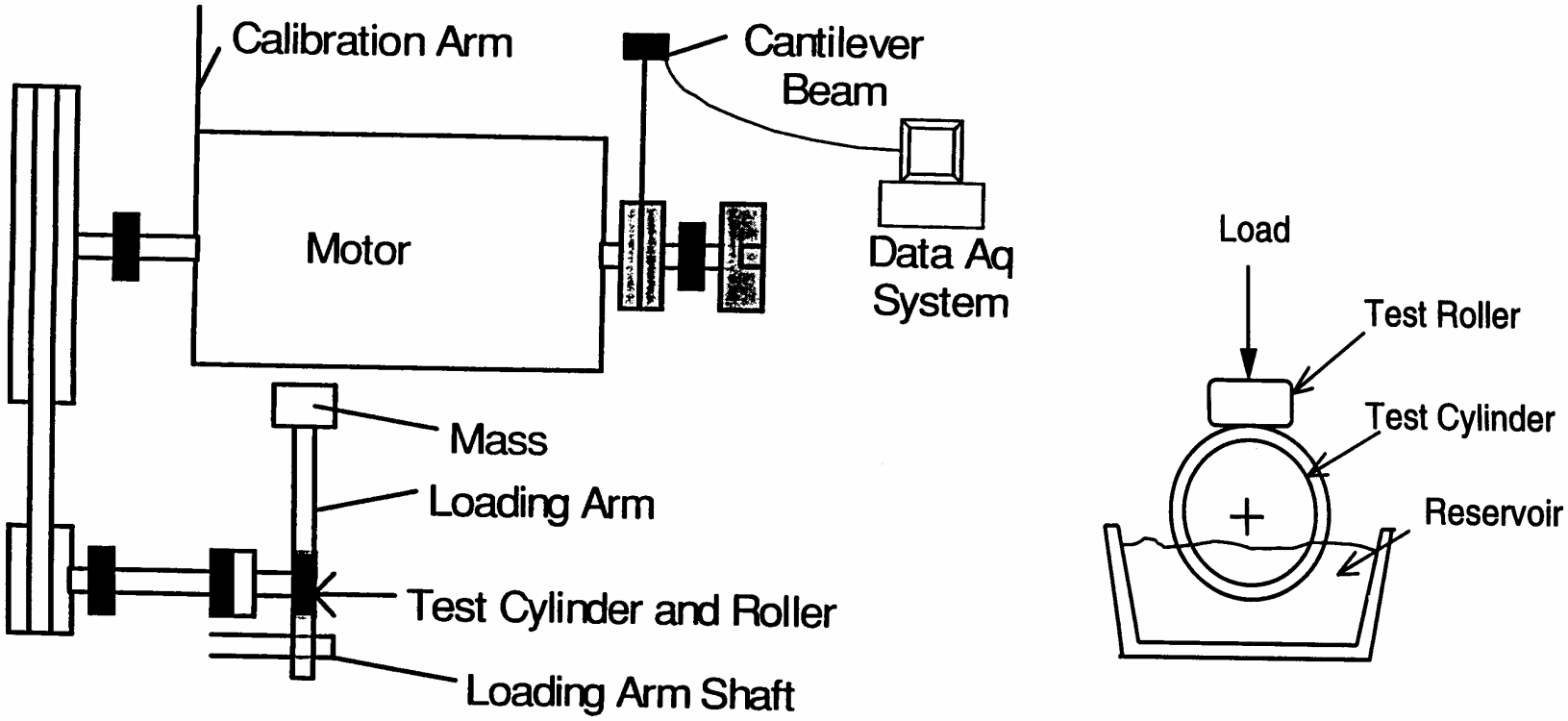
per the ASTM methods indicated in Table 3.2. First, 40 mL of liquid sample was placed in a test jar. The jar was then closed tightly with a cork carrying a test thermometer. The test jar was placed on the disc located on a gasket inside the jacket. The jacket was then filled with layers of ice and sodium sulfate in order to cool down the jacket. The test jar was then removed from the jacket periodically without disturbing the oil in order to inspect for cloud and pour points.

Boiling point is an important parameter for biodiesel as a fuel to be used in a diesel engine. Boiling point can be used to indicate the degree of contamination by high-boiling point materials such as un-reacted acylglycerols. A gas chromatograph – simulated distillation (Varian CP 3400 Gas chromatograph, specially configured for simulated distillation) was used to determine the boiling point distribution of purified esters.

Lubricity of the esters was measured by means of the Munson Roller on Cylinder Lubricity Evaluator (M-ROCLE). The M-ROCLE test apparatus is shown in Figure 3.2. The reaction torque was proportional to the friction force and was used to calculate the coefficient of friction. The image of wear scar area produced on the test roller was transferred to image processing software to measure wear scar area. The lubricity number (LN) was determined from steady state contact stress, Hertzian theoretical elastic contact stress, and coefficient of friction. The higher value of the lubricity number indicates the better lubricating property of the fuel. The detailed description for this method can be found in the literature (Lang et al., 2001b).

*3.2.5.2. Chemical characterization*

Purified esters were characterized for their chemical properties such as acid value,




(a) (b)

Figure 3.2: (a) The schematics of the M-ROCLE test apparatus; (b) Actual contact between the test roller and the cylinder (Lang et al., 2001b).

iodine value, saponification value, cetane index, and fatty acid compositions. Fatty acid components of esters were identified using gas chromatography - mass spectrometry (GC-MS, Varian, Saturn 2000) with a stable wax column. The fatty acid composition of purified esters was measured using a gas chromatography (GC, Agilent 6890) with a DB-23 column.

The acid value is defined as the mg of potassium hydroxide necessary to neutralize fatty acids in 1 g of sample and is measured as per AOCS official method Te 1a-64. It reflects the amount of free fatty acid content in biodiesel ester. Here, 5 g of the sample was accurately weighed and put into 500-ml Erlenmeyer flask. Then, 70-100 ml of 95% ethanol was poured into the flask which was heated on a hot plate. The solution was then agitated until a homogeneous solution was observed. Next, 0.5 ml of phenolphthalein indicator was added into the flask and the sample solution was titrated with 0.5 N NaOH. Titration volume was recorded at the point where the first pink color appeared and lasted for 30 seconds.

Saponification value is defined as the amount of alkali necessary to saponify a definite quantity of the sample. The procedure (according to AOCS method Cd 3-25) to determine saponification value is described as follows: First, 4-5 g of sample was weighed and put in to a 250-ml Erlenmeyer flask. Then, 50 ml of alcoholic KOH was poured into the flask, which was made to rotate gently. The flask was then connected with an air condenser and placed on a heating plate thus boiling the sample solution. A time of 1 h was required in order to completely saponify the sample. The flask and condenser were cooled and the interior surface of the air condenser was washed with a small amount of distilled water. The sample in the flask was titrated with 0.5 N HCl using

phenolphthalein as an indicator. Two blank runs were also conducted in the same manner without the oil sample using the procedure described above.

The iodine value is a measure of unsaturation of oils and is expressed in terms of the number of centigrams (cg) of iodine absorbed per g of sample (% iodine absorbed). When unsaturated oil is heated, polymerization of the triglyceride occurs which leads to gum formation. Also, unsaturated compounds are susceptible to oxidation when exposed to air, thereby degrading the oil quality. The higher iodine value indicates the higher degree of unsaturation of the corresponding oil. Approximately, 0.4 g of sample was weighed and placed in a 500-ml flask to which 20 ml of carbon tetrachloride was added as a solvent. Next, 25 ml of Wijs solution was pipetted into the flask and mixed properly and then stored in a dark place for 30 min. Then 25 ml of KI solution was added to the solution, followed by the addition of 100 ml of distilled water. The solution was then titrated with 0.1 N $Na_2S_2O_3$ solution using starch as an indicator. Two blank runs were also conducted simultaneously similar to the procedure as described above.

Cetane index is used to determine the ability of fuel to ignite quickly after being injected. This is an important property for biodiesel ester as a diesel fuel substitute. The cetane index was measured as per the correlation given by Krisnangkura (1986) as shown below.

Cetane index = 46.3 + 5458/saponification value – 0.225*Indine value … (3.2)

Cetane number is not much different from cetane index. The correlation reported by Patel (1999) is as given below:

Cetane number = cetane index –1.5 to +2.6. … (3.3)

## 3.3. Kinetic study of alkali-catalyzed transesterification of fryer grease

The effect of operating conditions on ester concentration and kinetics of alkali-catalyzed transesterification of fryer grease were studied. Reaction temperature, catalyst (KOH) concentration, and methanol to fryer grease molar ratio were varied in the range of 30-50 $^{o}$C, 0.5-1.5 wt%, and 6:1 to 12:1, respectively. Prior to the alkali-catalyzed transesterification reaction, the esterification of FFA present in fryer grease was carried out using an acid catalyst.

### *3.3.1. Esterification of free fatty acid in fryer grease*

Fryer grease (batch 2) obtained from Saskatoon Processing Company had an acid value and water content of 3.8 mgKOH·g$^{-1}$ and 0.5 wt%, respectively. A 100 g sample of the FG was placed in a Parr Reactor (Parr Instrument Company, Illinois, USA) and was heated to 60$^{o}$C. Methanol at the 3:1 methanol to fryer grease molar ratio and $H_2SO_4$ (1 % by weight with respect to fryer grease) were added to the FG. The esterification reaction was carried out with a stirring speed of 600 rpm at 60$^{o}$C for 2 hr. Then, the FG was washed with hot water in order to remove $H_2SO_4$ and unreacted alcohol. The trace amounts of moisture and alcohol were removed using the BÜCHI Rotavap in the same conditions as described in section 3.2.4. To ensure the complete removal of water, the fryer grease was then passed over anhydrous sodium sulfate. The fryer grease was then quite free of FFA and water and was ready for transesterification (FFA ~ 0.4 % and water content ~ 0.5 %).

### *3.3.2. Transesterification of neutralized fryer grease*

Transesterification of neutralized fryer grease with methanol was carried out in the temperature range of 30 - 50$^{o}$C using KOH as a catalyst. The methanol to oil ratio

and catalyst concentrations were varied at 6:1, 9:1, 12:1, and 0.5, 1.0, 1.5 % by weight, respectively. The transesterification of the FG was carried out using KOH as illustrated in Figure 3.3. For the characterization of biodiesel as a function of time, approximately 1.5 ml of reaction sample was collected each time in a measuring cylinder containing 3 drops of 1.1 N HCl acid solution in order to neutralize the alkaline catalyst. After collection of samples, they were immediately placed in an ice bath thus preventing further reaction from occurring. Samples were taken at 0.5 min time intervals for the first 2 min, and 1 min time intervals up to 10 min thereafter. After transesterification, each sample was diluted 20 times with tetrahydrofuran (THF) thus rendering a uniform mixture of transesterification products. The transesterification products were then analyzed using high performance liquid chromatograph (HPLC) located in the Department of Chemical Engineering, University of Saskatchewan.

*3.3.3. Analysis of products*

A Hewlett-Packard 1100 series HPLC equipped with a refractive index detector and Phenogel 5u 100A 300*7.80 mm 5 micron column protected with a guard column, and equipped with ChemStation for LC 3D, by Agilent Technologies was used to analyze transesterification products. THF was used as a mobile phase at 1 ml/min for 25 min. The operating parameters were as follows: injection volume 5 µl; column temperature 24 $^{o}$C; and detector temperature 35 $^{o}$C. Reference standard chemicals including methyl oleate, triolein, diolein, and monoolein were purchased from Sigma-Aldrich, MO, USA and were used to standardize the HPLC. The mono-, di-, triglyceride, and ester concentrations in transesterification products were analyzed using the HPLC. The glycerol concentration was calculated based on equations given by Komers et al. (2001).

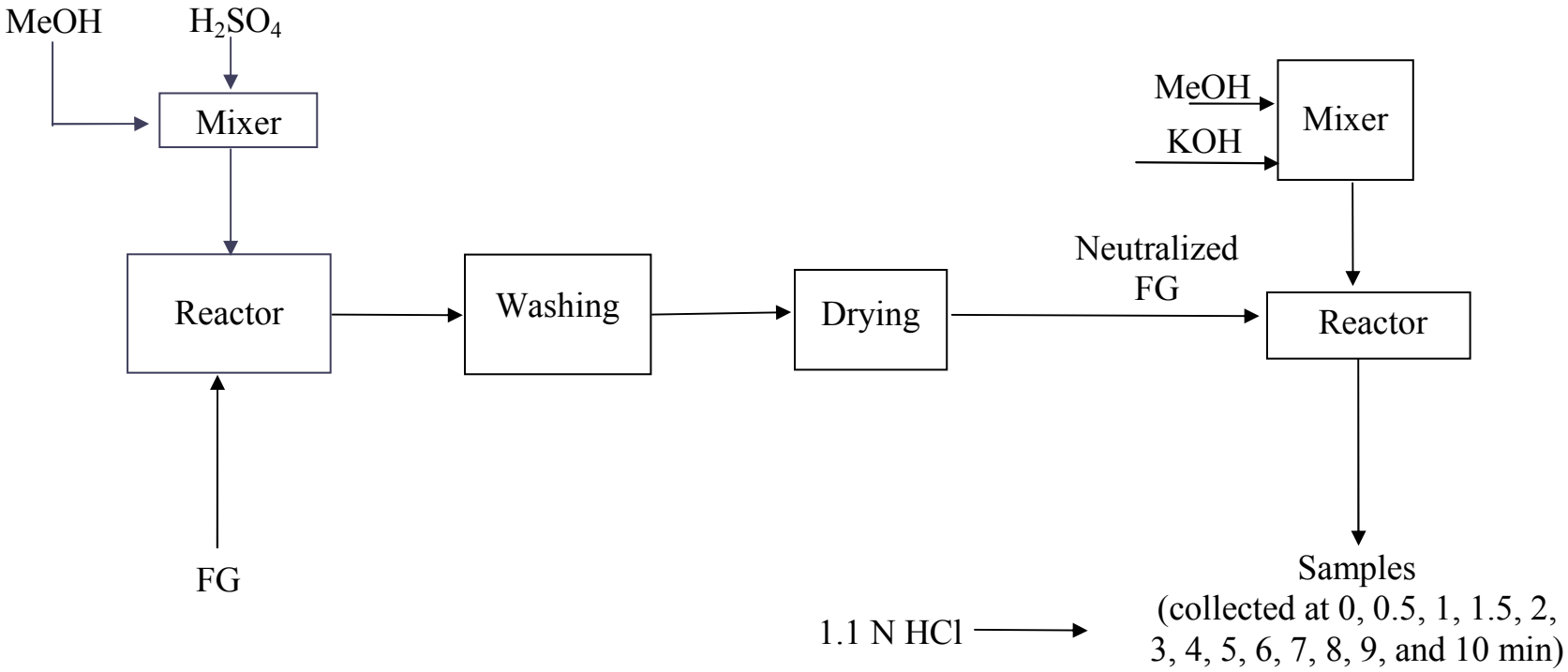



Figure 3.3: Flow chart for kinetic study of alkali-catalyzed transesterification of fryer grease.

The procedure for glycerol calculation is described in Appendix B.

*3.3.4. Kinetic modeling*

The mechanism proposed for transesterification of fryer grease is composed of a series of reversible decompositions of triglyceride to diglyceride, diglyceride to monoglyceride, and monoglyceride to glycerol (See Appendix C). Each step consumes 1 mole of alcohol and produces 1 mole of ester.

To determine the rate constants, differential equations were established by applying rate law in equations (C1)-(C6) (See Appendix C). Laplace transformation was used to solve the differential equations. Finally, the MATLAB program was used to compute the rate constants for each reaction. The MATLAB program, which was written for this study, can be found in Appendix D.

Activation energies for different steps were calculated based on Arrhenius equations as shown below,

$$k = Ae^{\frac{-E}{RT}} \quad \ldots (3.4)$$

$$\ln k = \ln A - \frac{E}{RT} \quad \ldots (3.5).$$

Where k = rate constant (the unit depends on the reaction order); A = pre-exponential factor (same unit as that of k); E = activation energy ($J \cdot mol^{-1}$); R = gas constant (8.314 $J \cdot mol^{-1} \cdot K^{-1}$); and T = temperature (K).

The kinetic results are described in section 4.5.

# 4. RESULTS AND DISCUSSION

## 4.1. Properties of crude fryer grease

Two batches of fryer grease (FG) with slight differences in quality (water content and acid value) were obtained from Saskatoon Processing Company. FG Batch One was used for the biodiesel synthesis and characterization study, and FG Batch Two was used in the kinetic study of alkali-catalyzed transesterification of FG.

The properties of FG Batch One are given in Table 3.1. In this batch, the initial water content was 7.3 wt. %, which was reduced to 0.2±0.1 wt. % after silica gel treatment. This crude FG contained 5.6% free fatty acid (FFA) which is much higher than that suitable for alkali-catalyzed transesterification (Freedman et al., 1984). Apart from water and FFA, the FG was contaminated with various other chemicals due to exposure to high temperatures for long periods of time during cooking hence, the total amount of polar molecules of the FG was 22%. Oxidized triglyceride content of the FG was 4.72%. This is due to oxidation of triglycerides in cooking oil at high temperatures for long time periods in the presence of air. For the same reason, some of the triglycerides got polymerized and the content of polymerized triglycerides in FG was 1.43%.

The FG Batch Two exhibited better qualities than FG Batch One, with water and FFA content of 0.5 wt. % and 7.6 wt. %, respectively. Both batches of FG required pre-treatment before being used as feedstock in the alkali-catalyzed transesterification process.

## 4.2. Process development for ester preparation

### *4.2.1. Transesterification of fryer grease using an alkaline catalyst*

Initially, FG was transesterified with methanol using KOH as a catalyst with a two-step transesterification process. The process was composed of 2 alkali-catalyzed transesterification steps, glycerol separation steps (after each transesterification step), and an ester purification step. This process proved to be successful for producing biodiesel from a high quality (fresh oil) feedstock (Lang et al., 2001a). The process involved 1 wt. % KOH (0.5 wt. % in each step), 6:1 methanol to oil molar ratio (3:1 in each step), 25 $^{o}$C as an operating temperature, and 30 min. of reaction time.

Glycerol could not be separated from the ester phase in the first step due to an interference of soap that had formed during the first transesterification step. The main factors responsible for this problem were high FFA and high water content in FG. The FFA reacts with KOH and forms soap while water partially favors the saponification reaction which consumes the catalyst and thereby reduces the biodiesel yield. Since glycerol could not be separated from the biodiesel ester, this process was considered unfeasible for this feedstock.

### *4.2.2. Production of biodiesel using a two-step (acid and alkali catalyzed) method*

FFA and water are problematic factors for transesterification using alkaline-type catalysts. Unlike water, which can easily be removed using silica gel, FFA in FG is difficult to eliminate. However, FFA can be converted into an ester by another esterification reaction using an acidic catalyst. In this research, initially, an acid-catalyzed esterification step was used. The FG was esterified with a 3:1 alcohol to oil molar ratio using 2 wt. % $H_2SO_4$ as a catalyst. The acid value of crude FG batch 1 was

11.2 (See Table 3.1). The acid value increased to 25.4 due to addition of $H_2SO_4$, which decreased to 15.8 after 5 hrs. of esterification and did not decrease any further within a time span of 9 hrs (See Table 4.1). The first step of esterification was stopped after this time in subsequent cases.

After the first step, the transesterification was carried out using KOH as a catalyst. The amount of ester collected after purification is as shown in Table 4.3. Transesterification with ethanol resulted in less biodiesel yield than those with methanol and mixed alcohol due to a stronger emulsion of ethanol, ethyl ester, and water which increased losses during the washing process. The experiments were conducted in two different ways: with and without silica gel treatment between the $1^{st}$ and $2^{nd}$ steps. The objective for the silica gel treatment was to remove trace amounts of water formed during the first esterification reaction step. If less water is present in FG, during alkali-catalyzed transesterification, a higher yield of biodiesel ester should be achieved. Table 4.2 shows that 30.0 – 45.5 g of biodiesel esters were produced from 50 g of FG. When the process with silica gel treatment between the $1^{st}$ and $2^{nd}$ step was used, a smaller amount of biodiesel was recovered than without the silica gel treatment. The total loss during the process plays an important role in rendering a lesser biodiesel yield. The total losses during the process with and without the additional silica gel treatment are 11.9 and 7.8 g for methanol and 33.2 and 25.8 g for ethanol, respectively. In the case of mixed alcohols, the total losses in experiments with the additional silica gel treatment are also higher than those without the treatment (See Table 4.2). The results show that losses caused by an additional step dominate the effect of water in alkali-catalyzed transesterification.

Table 4.1. Acid value change of FG Batch One during esterification reaction

| Reaction time [min] | Acid value [mgKOH·g$^{-1}$] |
|---|---|
| 0 | 11.2 |
| 1 | 25.4 |
| 60 | 18.0 |
| 120 | 17.5 |
| 300 | 15.8 |
| 480 | 15.8 |
| 540 | 15.8 |

Table 4.2. Mass balance on transesterification of fryer grease using the two-step process

| Experiment | Methanol to ethanol molar ratio | Input [g] | | | | | | Output [g] | | | Loss during the process* [g] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Fryer grease | Alcohol | $H_2SO_4$ | KOH | Glycerol† | Total | Ester | Glycerol | Total | |
| 1 | 6:0 | 50.3 | 11.6 | 1.0 | 1.6 | 2.5 | 67.0 | 41.1 | 18.1 | 59.2 | 7.8 |
| 2‡ | 6:0 | 50.9 | 11.7 | 1.0 | 1.6 | 0 | 65.2 | 38.4 | 14.9 | 53.3 | 11.9 |
| 3 | 5:1 | 50.7 | 12.2 | 1.0 | 1.6 | 4.5 | 70.0 | 44.6 | 19.1 | 63.7 | 6.3 |
| 4‡ | 5:1 | 50.6 | 12.0 | 1.0 | 1.6 | 3.1 | 68.3 | 33.0 | 20.3 | 53.3 | 15.0 |
| 5 | 4.5:1.5 | 51.2 | 12.5 | 1.0 | 1.6 | 3.9 | 70.2 | 45.5 | 18.3 | 63.8 | 6.4 |
| 6‡ | 4.5:1.5 | 50.3 | 12.6 | 1.0 | 1.6 | 3.4 | 68.9 | 30.0 | 20.6 | 50.6 | 18.3 |
| 7 | 4:2 | 50.0 | 12.9 | 1.0 | 1.7 | 4.2 | 69.8 | 43.2 | 19.6 | 62.8 | 7.0 |
| 8‡ | 4:2 | 49.8 | 12.9 | 1.1 | 1.6 | 4.2 | 69.6 | 33.5 | 20.2 | 53.7 | 15.9 |
| 9 | 3.5:2.5 | 50.4 | 13.2 | 1.0 | 1.7 | 4.8 | 71.1 | 42.6 | 22.2 | 64.8 | 6.3 |
| 10‡ | 3.5:2.5 | 50.2 | 13.3 | 1.0 | 1.6 | 6.6 | 72.7 | 32.8 | 24.1 | 56.9 | 15.8 |
| 11§ | 3:3 | 50.0 | 14.2 | 1.0 | 1.6 | 5.0 | 71.8 | 41.2 | 17.1 | 58.3 | 13.5 |
| 12§ | 3:3 | 50.3 | 14.2 | 1.0 | 1.6 | 7.8 | 74.9 | 37.5 | 21.0 | 58.5 | 16.4 |
| Average** | 3:3 | 50.2 | 14.2 | 1.0 | 1.6 | 6.4 | 73.4 | 39.4 | 19.1 | 58.4 | 15.0 |
| 13 | 0:6 | 50.7 | 16.6 | 1.0 | 1.6 | 7.1 | 77.0 | 34.6 | 16.6 | 51.2 | 25.8 |
| 14‡ | 0:6 | 50.0 | 16.6 | 1.1 | 1.6 | 6.0 | 75.3 | 31.0 | 11.1 | 42.1 | 33.2 |

* These losses occurred due to washing and transferring process.
† Pure glycerol added during separation process.
‡ Experiment with silica gel treatment after acid-catalyzed esterification of fryer grease.
§ Replicated experiment.
** Average value of experiment 11 and 12.

The ester yield originated from FG (60 – 91 %) is less than that originated from pure canola oil (95 – 97 %) (Lang et al., 2001a). Unlike fresh vegetable oils, FG is contaminated with diglyceride, monoglyceride, and other impurities. Therefore, FG contains a lesser number of moles of acyl-group, the actual origin of biodiesel ester, than a fresh vegetable oil does when an equal amount of oil is used as a feedstock.

The results from the replicated experiment were not appreciably different from each other (the differences between experiment 11 and 12 are only 3.7 g and 0.2 g for the ester and the total output, respectively) indicating that the experiments were reproducible.

*4.2.3. The glycerol separation process*

The purpose of using ethanol instead of methanol is to reduce dependency on a methanol producing petroleum source. When ethanol was used, glycerol could not be separated by gravity alone. Depending on how difficult the separation of glycerol from the ester was, various amounts of glycerol up to 7.8 g were added per 50 g of FG in order to separate glycerol from ester (See Table 4.2). However, the mixture of ethanol, ethyl ester, and glycerol formed very strong emulsion, therefore only 31.0-34.6 g of ester was recovered when 50 g of FG was used (See Table 4.3, Exp 13 and 14). In the case of methanol, separation of glycerol from the ester phase was much easier than that with ethanol. In the case of mixed methyl/ethyl esters, the addition of methanol was somewhat helpful in reducing ethanol concentration thus producing less emulsion. Therefore**,** more esters were obtained for these cases (See Table 4.2).

## 4.3. Ester characterization

All esters from FG were prepared, purified, and then characterized for their

physical and chemical properties as per the procedures described in Chapter 3.

*4.3.1. Physical charaterization*

The viscosity of FG was very high at 87.1 $mm^2/s$. This high value was due to the presence of higher molecular weight molecules such as triglycerides, polymerized triglycerides**,** and many other unknown heavier compounds formed during frying. After transesterification, esters showed substantial reduction in viscosity in the range of 4.7-5.9 $mm^2/s$, which met ASTM standard of 1.9-6.0 $mm^2/s$ (See Table 4.3).

There was not much difference in the viscosity of methyl, ethyl**,** and various mixtures of methyl/ethyl esters. The viscosity of biodiesel esters was in the range of 4.9-5.9 $mm^2/s$ which was higher than that of reference diesel #2 fuel (See Table 4.3). But at 5% addition of biodiesel to the diesel fuel (B5) the higher viscosity of biodiesel is not estimated to make any appreciable difference in the diesel engine performance. It is reported in the literature that methyl esters obtained from heated rapeseed oil have no negative influence on engine performance (Mittlebach and Enzelsberger, 1999).

The heating value of esters was not much different from their parent oil which ranged from 37.3 to 40.7 MJ/kg. These values were approximately 10% less than that of reference diesel #2 fuel (See Table 4.3). These data serve to indicate that approximately 10 wt. % more B100 biodiesel would be required in comparison with the regular diesel fuel to travel the same distance. There may be lubricity and oxygenate benefits for B100 to counteract this loss in heating value.

The cloud point of esters was in the range of 1 to -2 $^oC$ while pour point range was -3 to -6 $^oC$. The cloud point and pour points of the reference diesel fuel #2 were -5 and –15 $^oC$, respectively, which were much lower than those of fryer grease esters

Table 4.3. Heating value, viscosity, cloud point, and pour point of fryer grease esters prepared at 50 $^{o}$C for methyl and mixed methyl-ethyl esters and 60 $^{o}$C for ethyl esters as compared to those of diesel fuel #2 and ASTM standard

| Sample | Heating value [MJ/kg] | Viscosity @40$^{o}$C [mm$^2$/s] | Cloud point [$^{o}$C] | Pour point [$^{o}$C] |
|---|---|---|---|---|
| FG | 40.2 | 87.1 | - | - |
| FME* | 37.3 | 4.7 | 1 | -3 |
| FEE† | 40.7 | 5.0 | -2 | -6 |
| FMEE (3:3)‡ | 40.1 | 5.9 | -1 | -4 |
| FMEE (3.5:2.5) | 40.0 | 5.4 | -1 | -4 |
| FMEE (4:2) | 40.0 | 5.0 | 0 | -4 |
| FMEE (4.5:1.5) | 40.1 | 5.4 | 0 | -4 |
| FMEE (5:1) | 39.8 | 4.9 | 1 | -3 |
| Diesel#2 | 45.5 | 3.5 | -5 | -15 |
| ASTM | N/A§ | 1.9-6.0 | N/A | N/A |

* FME – Fryer grease methyl ester.
† FEE – Fryer grease ethyl ester.
‡ FMEE – Fryer grease methyl-ethyl ester prepared using 3:3 molar ratio of methanol and ethanol, with a total 6:1 alcohol to oil molar ratio.
§ Not available.

(See Table 4.3). Higher cloud and pour point of esters may be due to the presence of polymerized esters during transesterification. There was a decrease in cloud and pour point of mixed esters with a decrease in molar ratio of methanol to ethanol. The cloud and pour point of methyl ester was higher than the corresponding ethyl ester. These results fit well with the previous work (Lang et al., 2001a). From these results it is clear that fryer grease derived esters would be a suitable candidate as a diesel fuel substitute in tropical countries and not as suitable at B100 in colder climate conditions such as in Canada. However, weaker blends (B5), winterization of FG**,** or some additives may assist the application of esters in colder temperatures.

The lubricity property of the esters was measured via the M-ROCLE test method at the Department of Mechanical Engineering, University of Saskatchewan. Only 1 vol. % of the various esters was added to a kerosene base fuel and the lubricity was measured. Properties of the kerosene base fuel are shown in Appendix E. The coefficient of friction, wear scar area, and lubricity number of kerosene base fuel treated at 1 vol.% of fryer grease methyl ester (FME), fryer grease ethyl ester (FEE), and fryer grease methyl ethyl ester (FMEE, 3:3 methanol to ethanol molar ratio) are shown in Table 4.4. All three of these esters showed substantial improvements in the lubricity. With 1 vol % addition of the ester to kerosene base fuel, the lubricity numbers of the treated fuel increased by 18.7, 33.0, and 19.4 %, respectively (See Table 4.4). The wear scar and coefficient of friction also decreased substantially by the addition of 1 vol. % of fryer grease esters in kerosene. Table 4.5 shows boiling points of pure esters commonly found in biodiesel (J.W. Goodrum, 2002). The values in this table illustrate an increase in boiling point with molecular weight.

Table 4.4. M-ROCLE lubricity tests for esters prepared from fryer grease

| Fuel additive (1% vol. in kerosene) | Coefficient of friction | Wear scar area ($mm^2$) | Lubricity number | % increase in lubricity number |
|---|---|---|---|---|
| BASE | 0.117 | 0.338 | 0.689 | - |
| FME | 0.114 | 0.294 | 0.818 | 18.7 |
| FMEE (3:3) | 0.114 | 0.265 | 0.916 | 33.0 |
| FEE | 0.113 | 0.293 | 0.823 | 19.4 |

Table 4.5. Boiling points of pure methyl esters at 1 atm (100 kPa) (J.W. Goodrum, 2002)

| Composition | CAS registry number | Boiling point ($^{o}$C) |
|---|---|---|
| Methyl undecanoate (C11:0) | 1731-86-8 | 248 |
| Methyl laurate (C12:0) | 111-82-0 | 262 |
| Methyl myristate (C14:0) | 124-10-7 | 296 |
| Methyl palmitate (C16:0) | 112-39-0 | 415 |
| Methyl stearate (C18:0) | 112-61-8 | 442 |
| Methyl oleate (C18:1)* | 112-62-9 | 218 |

* Measured at 2.66 kPa.

Boiling point distributions of FG, fryer grease esters, diesel fuel**,** and kerosene base fuel were measured using a gas chromatograph – simulated distillation located at the Department of Chemical Engineering, University of Saskatchewan, and are shown in Figure 4.1. FG showed higher boiling points than its esters, i.e., fryer grease methyl ester, fryer grease ethyl ester, and fryer grease methyl-ethyl ester {FMEE (3:3)}. This can be explained by the fact that large molecules, such as acylglycerols and polymerized materials present in FG got converted into smaller molecules, i.e. esters after transesterification, and glycerol, which was separated (Mittelbach and Enzelsberger, 1999). Since all esters were prepared from FG, boiling point distributions of all the esters did not show a significant difference. Diesel fuel and kerosene were more volatile than fryer grease esters and the boiling point of kerosene was lower than those of the esters (See Figure 4.1). But "at 90% off", the boiling points of FG esters matched with that of diesel fuel. This implies that biodiesel prepared from FG can be burnt in a conventional diesel engine without further modification.

*4.3.2. Chemical charaterization*

Fatty acid components of FG esters were detected by GC-MS (see Figures 4.2, 4.3, and 4.4). This analysis showed that major fatty acid components in all esters are myristic acid (C14:0), palmitic acid (C16:0), palmitoleic acid (C16:1), stearic acid (C18:0), oleic acid (C18:1), linoleic acid (C18:2), linolenic acid (C18:3), arachidic acid (C20:0), eicosenoic (C20:1), and behenic acid (C22:0) with the major contribution from oleic acid in all the esters (See Table 4.6). Figure 4.4 indicates that when FG was transesterified with a mixture of methanol/ethanol (3:3), ethyl esters were also formed,

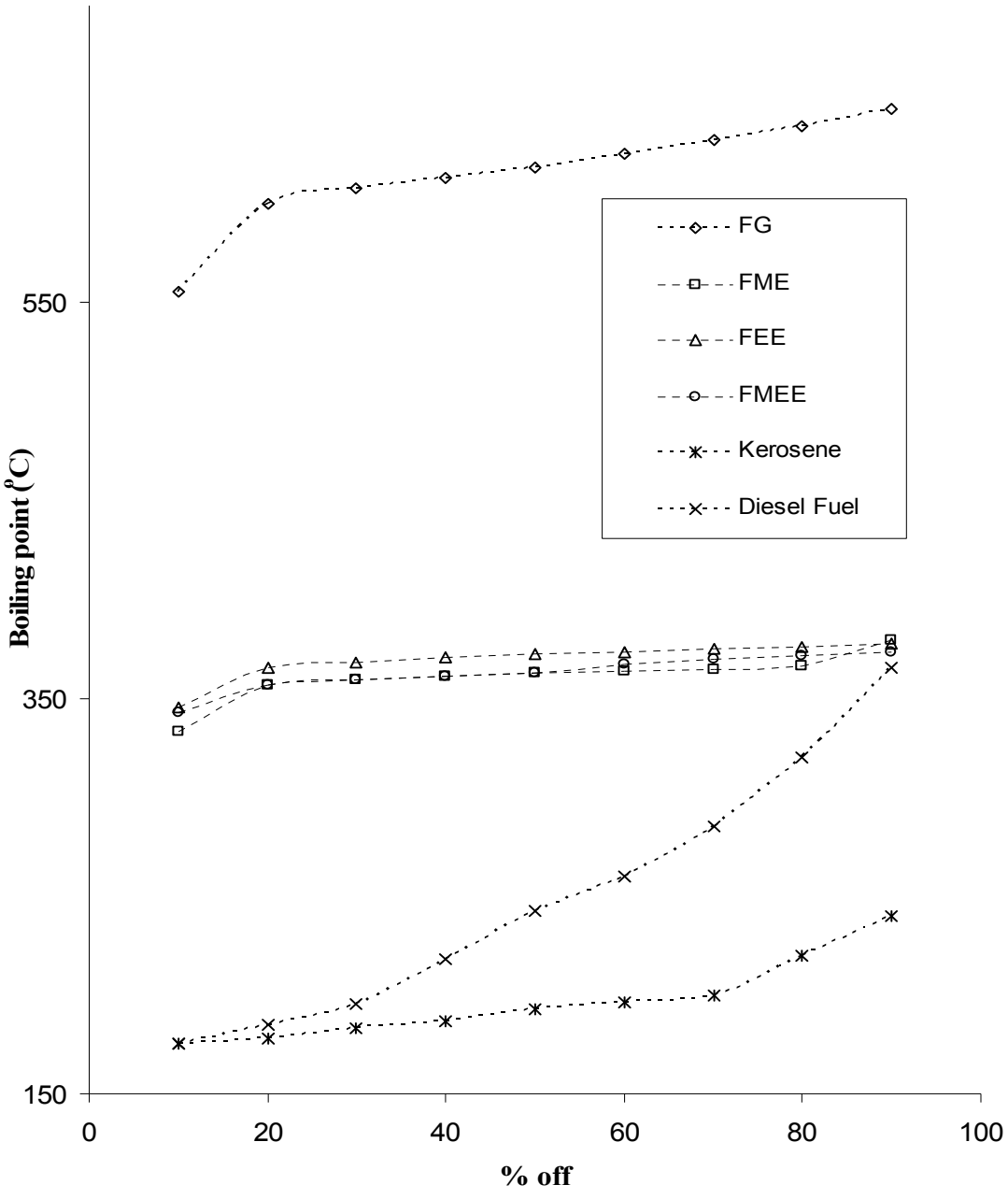



Figure 4.1: Boiling point vs. % off of fryer grease, fryer grease methyl ester, fryer grease ethyl ester and fryer grease methyl ethyl ester (FMEE (3:3)).

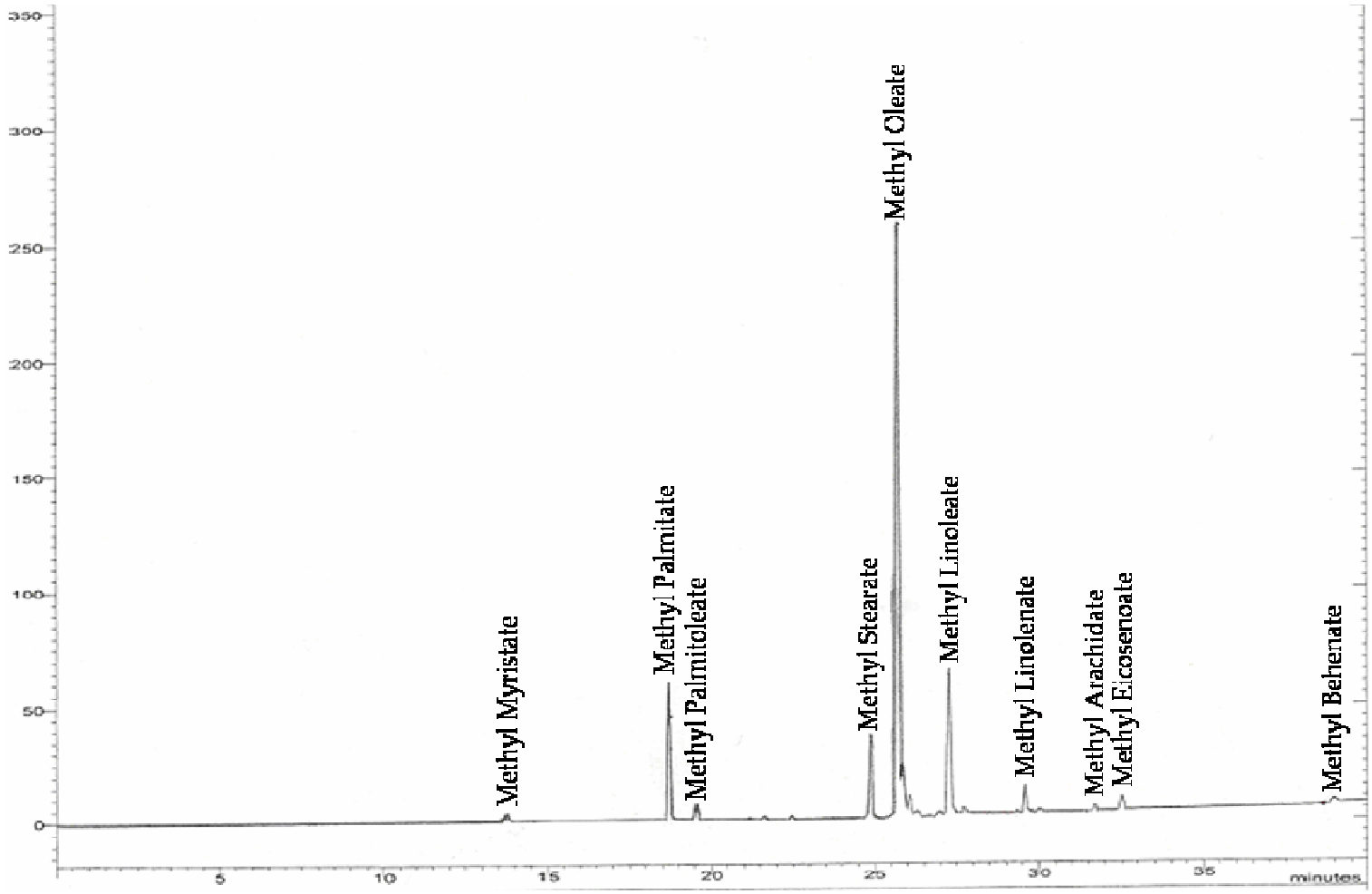



Figure 4.2: GC-MS chromatogram of fryer grease methyl ester (FME).

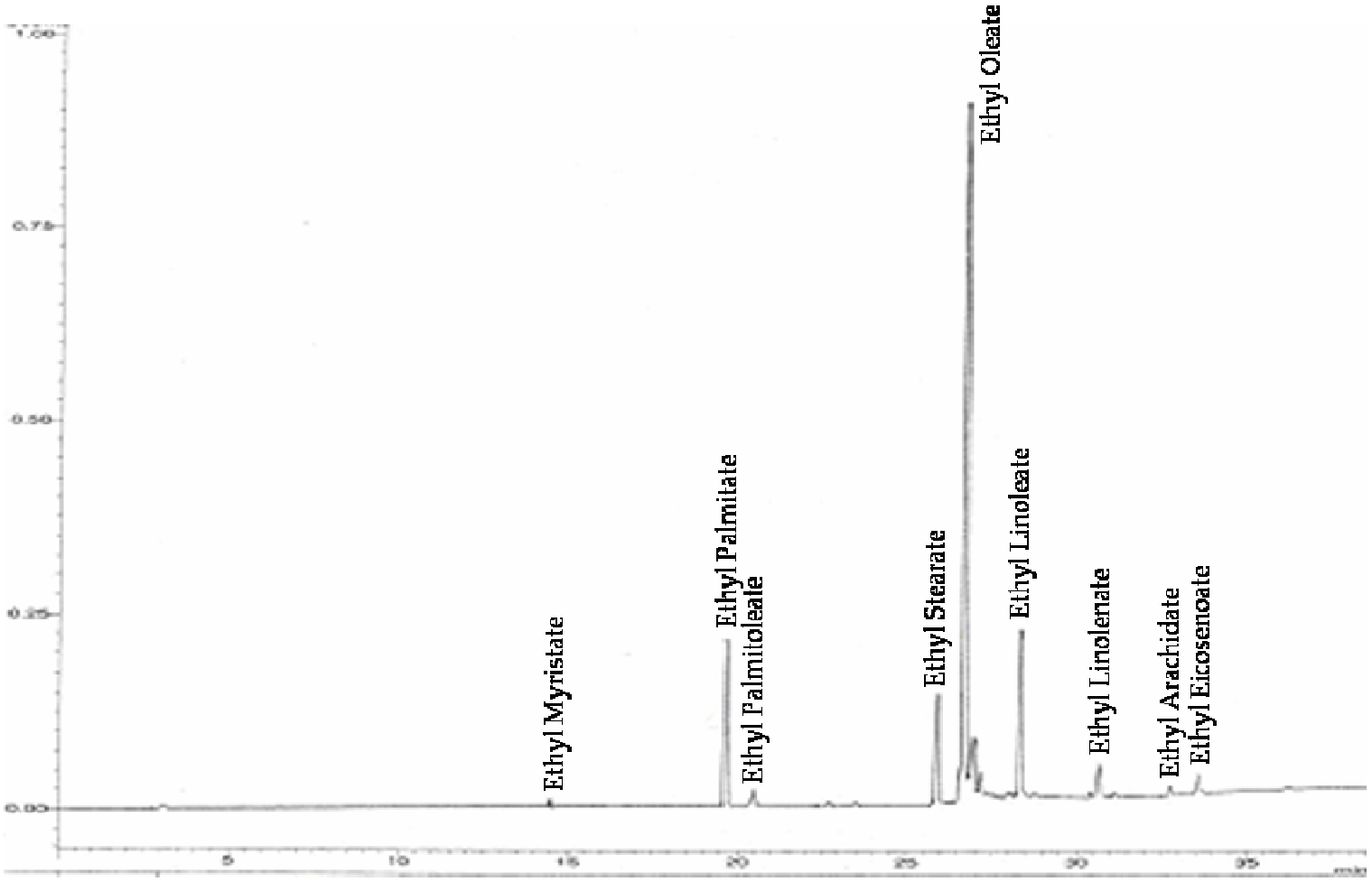



Figure 4.3: GC-MS chromatogram of fryer grease ethyl ester (FEE).

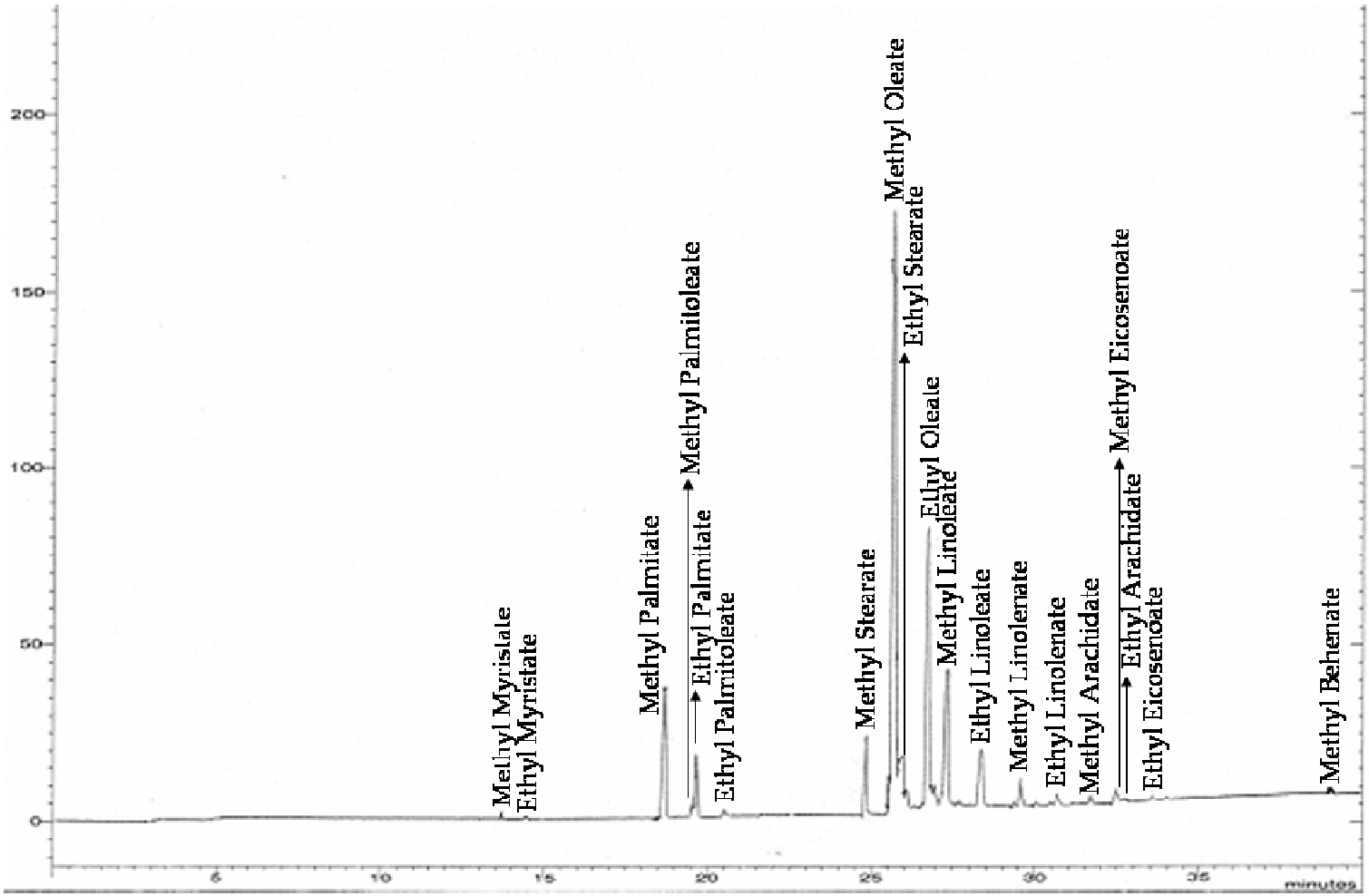



Figure 4.4: GC-MS chromatogram of fryer grease methyl ethyl ester (FMEE (3:3)).

along with methyl esters. A similar observation was also made with other mixtures of methanol and ethanol.

The fatty acid composition of all the esters is presented in Table 4.6. All of these esters showed oleic acid (~51.1%) as the dominant fatty acid. Oleic acid was also found to be a major fatty acid of esters prepared from canola oil by Lang et al. (2001a) indicating that the FG was derived from canola oil. In case of FMEE (3:3), ethyl esters formed during transesterification were approximately 45% of those of methyl esters i.e., the formation of ethyl esters was less compared to methyl. This can be explained by the fact that the reactivity of methoxide ions is higher than that of ethoxide ions (Sridharan and Mathai, 1974).

In the case of esters formed by the reaction of FG with 3.5:2.5, 4:2, 4.5:1.5, 5:1 molar ratio of methanol to ethanol, the percentage of ethyl esters of various fatty acids formed are compared to methyl esters (See Table 4.6). When the methanol to ethanol molar ratio was increased, less ethanol molecules were available for transesterification and ultimately less ethyl esters were formed.

The acid value of crude FG was very high (See Table 4.7) but by using the two-step method, the acid value of esters derived from FG was reduced substantially and was within the limit of ASTM standard (0.8 mgKOH $\cdot g^{-1}$) as shown in Table 4.7. This is because FFA initially contained in FG was converted into biodiesel ester, which reduced the acid values of the transesterification products.

The origin of the oil is the major factor affecting the iodine value of the esters. Iodine value of FG was 94.5 cg iodine/g FG (See Table 4.7). Since all the esters were prepared from FG, iodine values of the esters were close to that of the FG and were in the

Table 4.6. Fatty acid composition (wt%) of esters derived from fryer grease

| Fatty acid | | FME | FEE | FMEE (3:3) | FMEE (3.5:2.5) | FMEE (4:2) | FMEE (4.5:1.5) | FMEE (5:1) |
|---|---|---|---|---|---|---|---|---|
| Myristic (C14) | methyl | 0.42 | | 0.33 | 0.32 | 0.33 | 0.37 | 0.39 |
| | Ethyl | | 0.41 | 0.19 | 0.18 | 0.15 | 0.11 | 0.11 |
| Palmitic (C16) | methyl | 8.64 | | 6.66 | 6.56 | 6.90 | 7.50 | 7.83 |
| | ethyl | | 8.22 | 2.46 | 2.32 | 1.91 | 1.26 | 0.94 |
| Palmitoleic (C16:1) | methyl | 0.91 | | 0.67 | 0.68 | 0.73 | 0.79 | 0.83 |
| | ethyl | | 0.89 | 0.34 | 0.32 | 0.26 | 0.24 | 0.16 |
| Stearic (C18) | methyl | 5.92 | | 4.26 | 4.52 | 4.74 | 5.15 | 5.35 |
| | ethyl | | 5.61 | 2.48 | 2.31 | 2.07 | 1.69 | 1.49 |
| Oleic (C18:1) | methyl | 51.12 | | 36.96 | 38.30 | 40.63 | 44.15 | 46.07 |
| | ethyl | | 48.83 | 14.57 | 13.73 | 11.39 | 7.58 | 5.67 |
| Linoleic (C18:2) | methyl | 11.68 | | 9.01 | 9.68 | 10.14 | 10.73 | 10.98 |
| | ethyl | | 10.94 | 3.69 | 3.37 | 2.89 | 2.06 | 1.65 |
| Linolenic (C18:3) | methyl | 2.98 | | 2.08 | 2.19 | 2.38 | 2.62 | 2.71 |
| | ethyl | | 2.68 | 0.87 | 0.77 | 0.66 | 0.48 | 0.37 |
| Arachidic (C20) | methyl | 0.59 | | 0.42 | 0.44 | 0.48 | 0.53 | 0.53 |
| | ethyl | | 0.56 | 0.18 | 0.17 | 0.14 | 0.10 | 0.09 |
| Eicosenoic (C20:1) | methyl | 1.02 | | 0.73 | 0.78 | 0.81 | 0.90 | 0.94 |
| | ethyl | | 0.97 | 0.31 | 0.28 | 0.22 | 0.15 | 0.12 |
| Behenic (C22:1) | methyl | 0.31 | | 0.21 | 0.24 | 0.24 | 0.27 | 0.27 |
| | ethyl | | N.I.* | N.I. * | N.I. * | N.I. * | N.I. * | N.I. * |
| Others | | 16.41 | 20.89 | 13.58 | 12.84 | 12.93 | 13.32 | 13.50 |

* Not identified.

Table 4.7. Chemical properties of fryer grease and esters derived from fryer grease

| Sample | Acid value [mgKOH/g] | Iodine value [cg iodine/g] | Saponification value [mgKOH/g] | Cetane index |
|---|---|---|---|---|
| FG | 11 | 94.5 | 174.5 | 55.7 |
| FME | 0.5 | 85.8 | 174.4 | 58.3 |
| FEE | 0.8 | 82.6 | 169.7 | 59.9 |
| FMEE (3:3) | 0.7 | 84.6 | 171.4 | 59.1 |
| FMEE (3.5:2.5) | 0.6 | 81.4 | 170.7 | 60.0 |
| FMEE (4:2) | 0.7 | 82.4 | 172.3 | 59.4 |
| FMEE (4.5:1.5) | 0.4 | 82.7 | 173.8 | 59.1 |
| FMEE (5:1) | 0.3 | 83.2 | 174.5 | 58.9 |

range of 81.4 to 85.8 as shown in Table 4.7. Different molar ratios of methanol and ethanol used during reaction did not indicate a significant impact on iodine value. A higher iodine value of 211 of esters derived from linseed oil was reported (Lang et al., 2001a). This is because the major fatty acids present in linseed oil (linolenic, C18:3) are more unsaturated than that contained in FG. Iodine value of conventional diesel fuel was approximately 10 (Lang et al., 2001a). This implies that diesel engine utilizing biodiesel is more susceptible to gum formation than that utilizing conventional diesel fuel due to the higher iodine values of biodiesel.

From Table 4.7, saponification values of esters were within the range of 169.7 to 174.5. There was no significant difference in saponification value among esters prepared from FG. Also, saponification values of esters prepared from FG were not different from that of their parent oil (FG). The average molecular weight of oil can be calculated by multiplying the inverse of saponification value by 168000 (Obibuzor et al., 2003). Therefore, the higher the saponification value, the lower the molecular weight. According to Welch, Holme & Clark Co., Inc. (2006), the saponification value of canola oil is in the range of 188-198. This indicates that the molecular weight of FG is higher than that of canola oil due to polymerized acylglycerols formed during the frying process, which agrees with the facts discussed earlier in this chapter. Saponification values of esters prepared from different plants were reported as 201.1, 201.4, 202.6, 196.7, and 198.6 for *Azadirachta indica, Calophyllum inophyllum, Jatropha curcas, Pongamia pinnata,* and *Ziziphus* mauritiana, respectively (M. Mohibbe Azam et al., 2005). The results from Table 4.7 show that saponification values of esters prepared from FG (170.7-174.5) are less than those prepared from fresh oils. This indicates that esters prepared

from FG have higher molecular weight than those prepared from fresh oil. Polymeric esters were the possible compounds found in esters derived from FG, which are responsible for the higher average molecular weight of FG ester compared to that of fresh oil (Mittelbach and Enzelsberger, 1999).

The cetane index of all the esters prepared from FG was within the range of 58.3 to 60.0 as shown in Table 4.7. The cetane index of methyl, ethyl and various mixtures of methyl/ethyl esters was almost the same. According to the correlation given by Patel (1999) (also See Section 3.2.5.2), all esters meet the ASTM standard {D 6751-02} (≥47) specified for the cetane number (See Appendix A). Hence, it is clear that all the esters prepared from FG have good combustion quality. In fact, it was reported that blends and pure esters derived from waste vegetable oil would help a diesel engine to perform more efficiently than with diesel fuel (Al-Widyan et al., 2002).

## 4.4. Process optimization

The objective of this study was to optimize the conditions for transesterification of FG for higher ester yield. The effects of catalyst concentration, reaction temperature, and alcohol-to-oil molar ratio were included in this study. Stirring speed of all experiments was fixed at 600 rpm. Table 4.8 summarizes the effects of catalyst concentration, reaction temperature, and alcohol-to-oil molar ratio in terms of conversion. The sample calculation on conversion is given in Appendix B.

The detailed procedure used in this study was explained in section 3.3 and the rate constants and activation energies can be referred to in section 4.5.

### *4.4.1. Effect of catalyst loading*

Table 4.8. The % conversion of alkali-catalyzed transesterification of fryer grease

| Run | Catalyst concentration [wt. %] | Temperature [$^{o}$C] | Alcohol to oil molar ratio | Conversion, mol % | | |
|---|---|---|---|---|---|---|
| | | | | 1 min | 5 min | 10 min |
| 1 | 0.5 | 30 | 6:1 | 16.5 | 44.5 | 53.6 |
| 2 | 0.5 | 40 | 6:1 | 27.5 | 61.8 | 66.0 |
| 3 | 0.5 | 50 | 6:1 | 34.6 | 66.6 | 71.6 |
| 4 | 1.0 | 30 | 6:1 | 61.5 | 76.8 | 84.3 |
| 5 | 1.0 | 40 | 6:1 | 72.5 | 81.9 | 83.6 |
| 6 | 1.0 | 50 | 6:1 | 75.4 | 82.2 | 84.1 |
| 7 | 1.5 | 30 | 6:1 | 81.7 | 86.8 | 90.1 |
| 8 | 1.5 | 40 | 6:1 | 78.9 | 87.3 | 90.0 |
| 9 | 1.5 | 50 | 6:1 | 81.5 | 90.4 | 99.9 |
| 10 | 1.0 | 30 | 9:1 | 35.8 | 65.4 | 78.0 |
| 11 | 1.0 | 40 | 9:1 | 42.4 | 78.0 | 86.1 |
| 12 | 1.0 | 50 | 9:1 | 55.3 | 83.7 | 89.5 |
| 13 | 1.0 | 30 | 12:1 | 21.0 | 48.2 | 70.2 |
| 14 | 1.0 | 40 | 12:1 | 45.2 | 73.6 | 83.7 |
| 15 | 1.0 | 50 | 12:1 | 52.5 | 86.1 | 92.7 |

The catalyst loading (KOH) was varied from 0.5 to 1.5 wt.% in this study. Figures 4.5, 4.6, and 4.7 show ester concentration distribution using 6:1 alcohol to oil molar ratio at 30, 40, and 50 $^{o}$C, respectively. To avoid the escape of methanol into a gas phase during the reaction, the reaction temperatures were maintained 10 $^{o}$C below boiling point of methanol. Hence, the reaction temperatures of 30, 40, and 50 $^{o}$C were chosen for this study.

The results show that ester concentrations increase with catalyst loading. This is a typical observation which agrees with the literature (Zhou et al., 2003). However, the rate of the increase in ester concentration dropped when catalyst concentration was increased beyond 1 wt. %. In addition, the conversion increased as catalyst concentration increased. Hydroxide ions from KOH react with the methanol molecule and produce methoxide ions (See Pre-step Figure 2.3), therefore the rate of reaction increases when hydroxide concentration is increased.

From Figures 4.5, 4.6, and 4.7, the rate of ester formation increased significantly when catalyst concentration was increased from 0.5 to 1.0 wt.%. However, further increases in catalyst concentration from 1.0 to 1.5 wt.% did not show any significant improvement in the rate of ester formation, therefore the optimum catalyst concentration for transesterification of FG was determined to be 1.0 wt.% KOH.

*4.4.2. Effect of reaction temperature*

The effect of reaction temperature on ester concentration was studied at 6:1, 9:1, and 12:1 methanol to oil molar ratios using 0.5, 1.0, and 1.5 wt. % KOH. Figures 4.8 and 4.9 show an ester concentration profile of transesterification of fryer grease with 6:1 alcohol to oil molar ratio using 0.5 % KOH and with 9:1 alcohol to oil molar ratio using

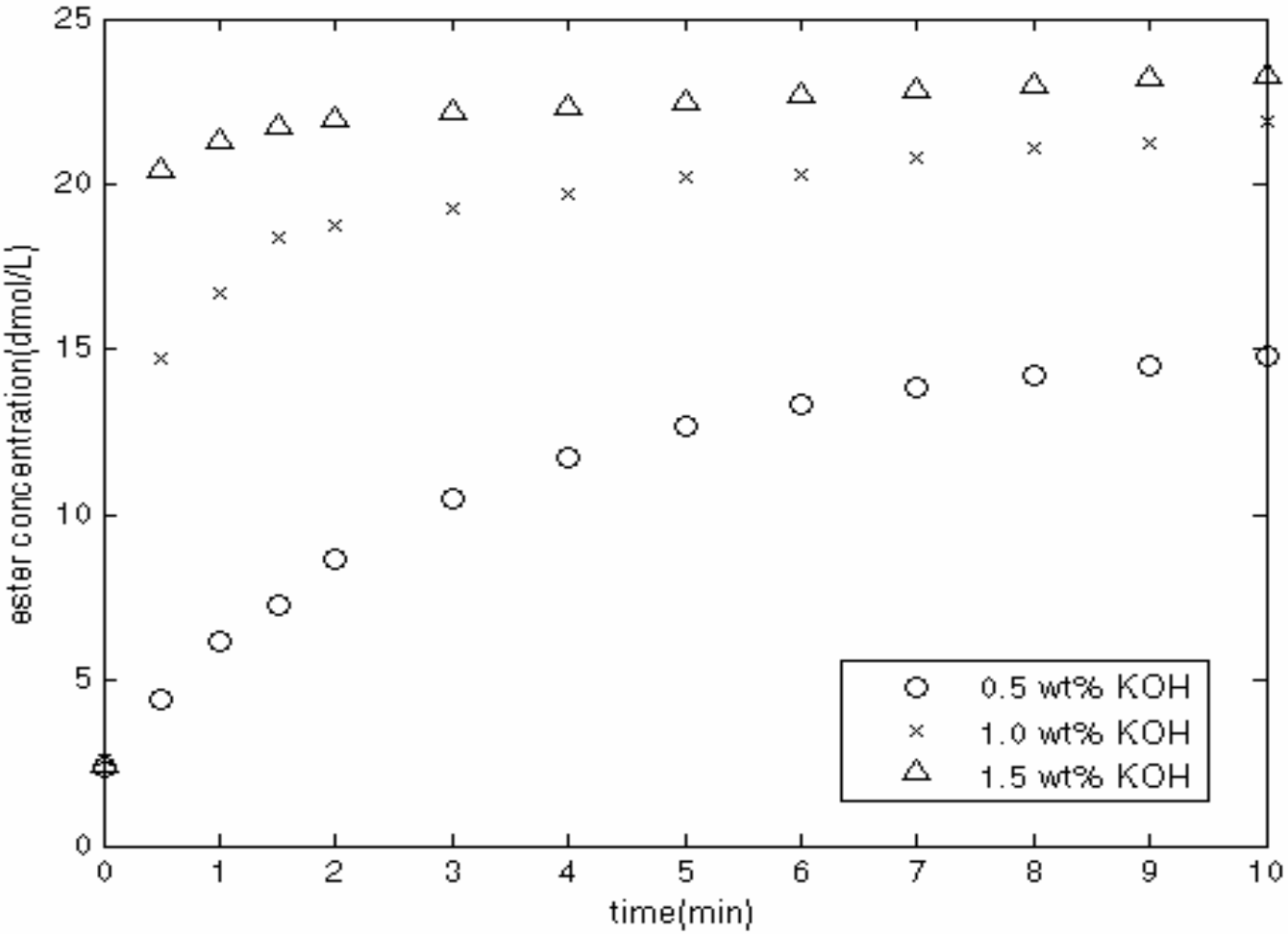



Figure 4.5: Effect of catalyst loading on ester concentration with 6:1 methanol to oil molar ratio at 30 $^{o}$C.

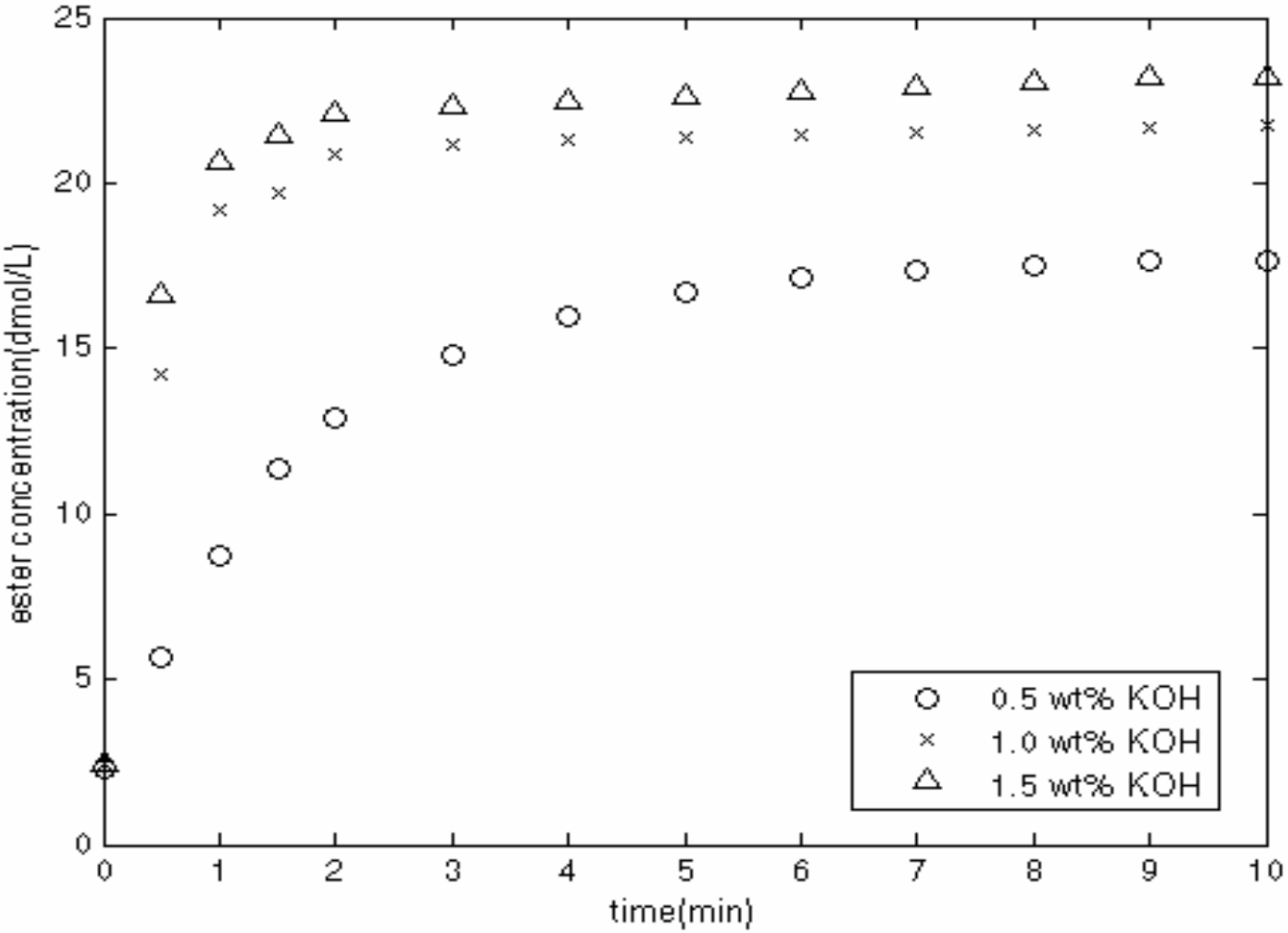



Figure 4.6: Effect of catalyst loading on ester concentration with 6:1 methanol to oil molar ratio at 40 $^{o}$C.

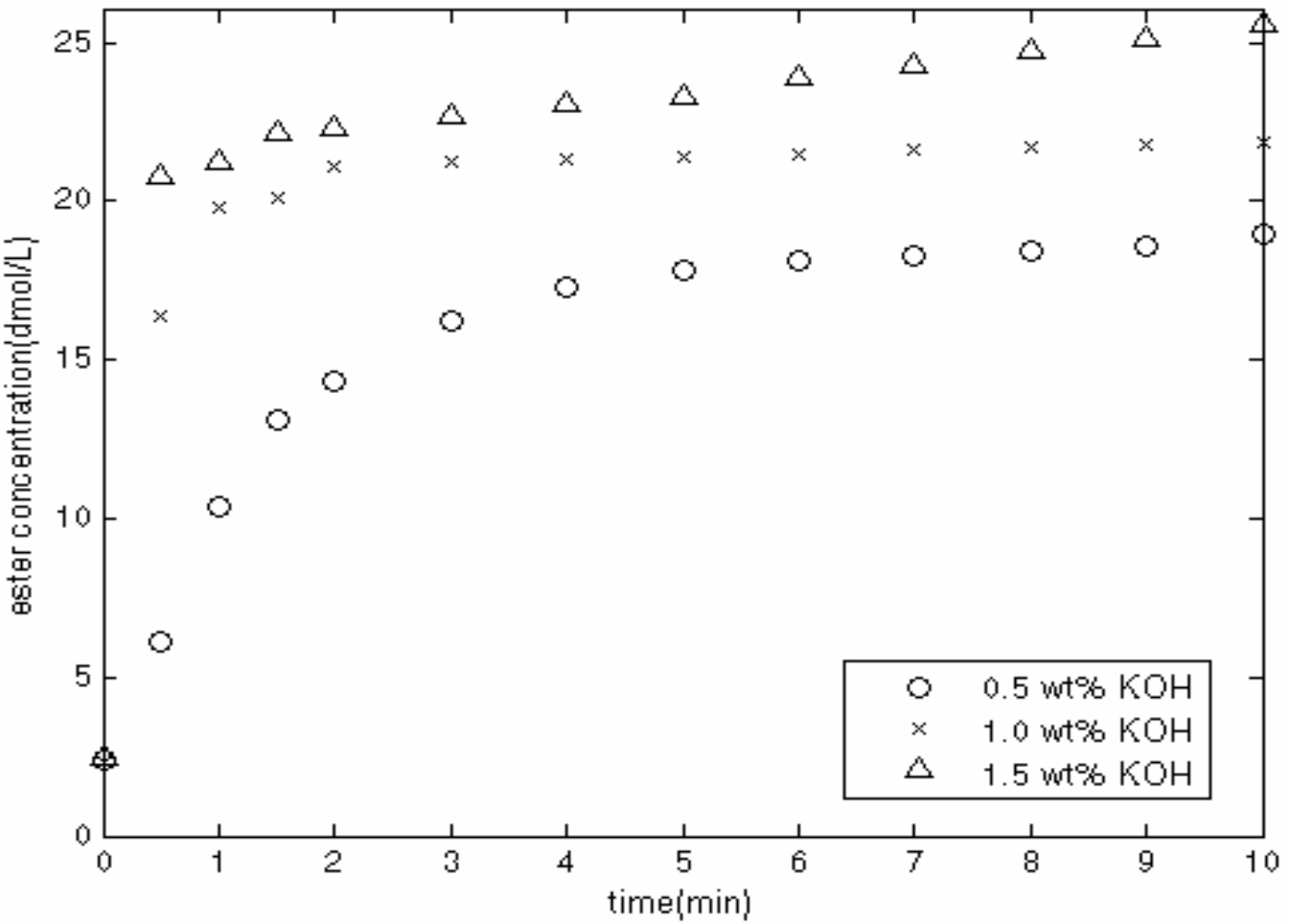



Figure 4.7: Effect of catalyst loading on ester concentration with 6:1 methanol to oil molar ratio at 50 $^{o}$C.

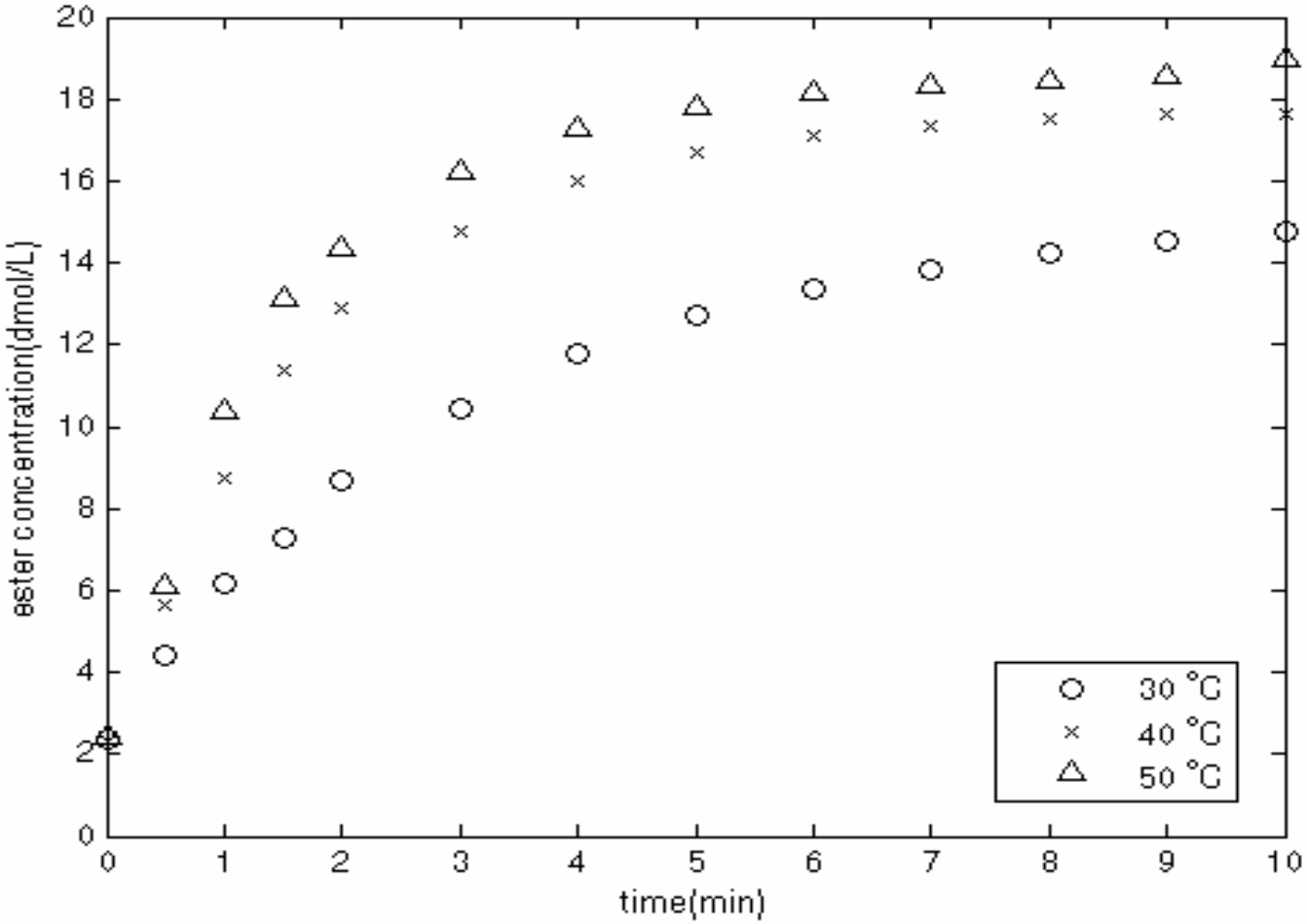



Figure 4.8: Effect of reaction temperature on ester concentration with 6:1 methanol to oil molar ratio using 0.5 wt. % KOH.

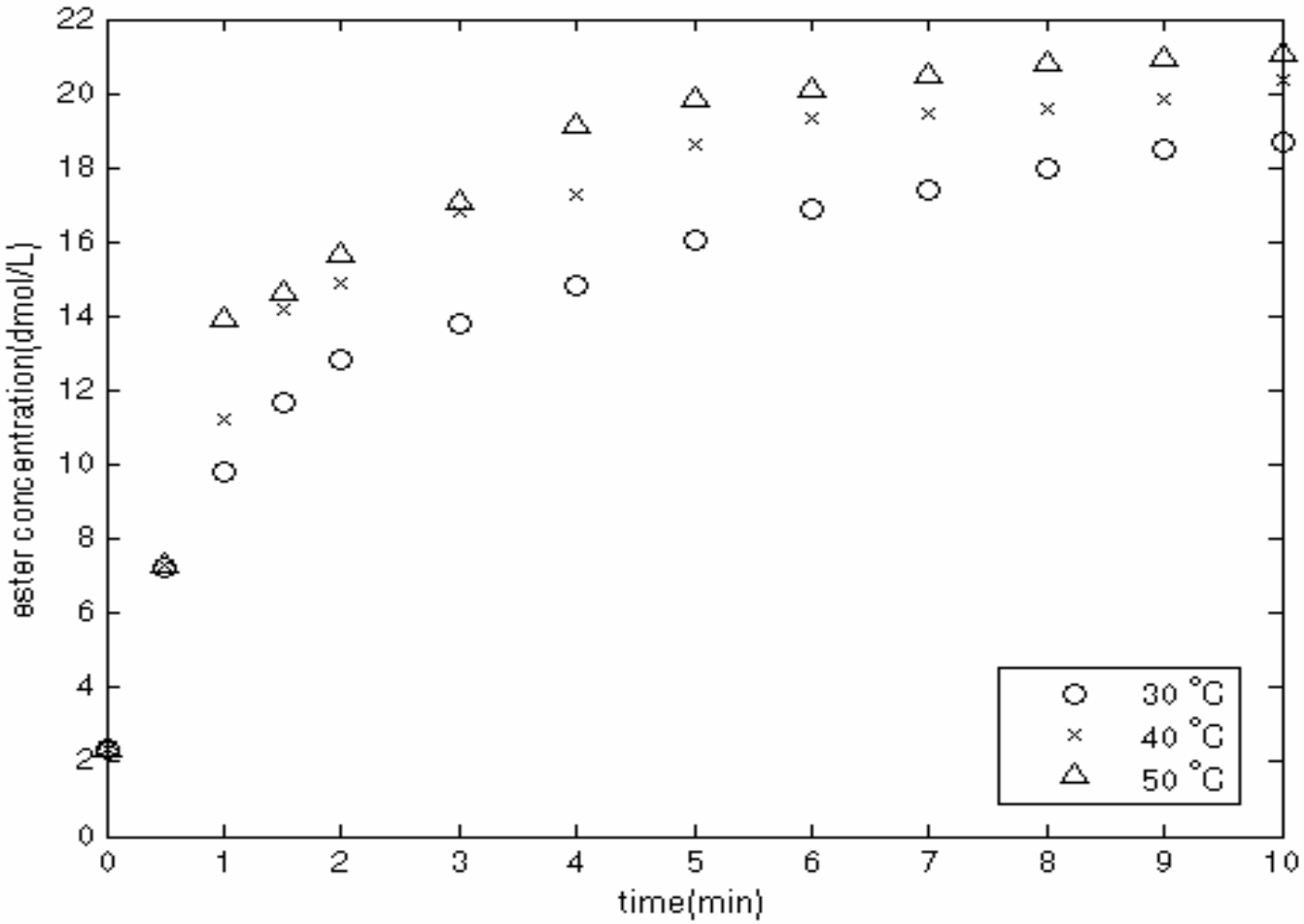



Figure 4.9: Effect of reaction temperature on ester concentration with 9:1 methanol to oil molar ratio using 1.0 wt. % KOH.

1.0 % KOH, respectively.

It is evident from these figures that the higher ester formation rate is favored by higher reaction temperatures. Also, Table 4.8 illustrates higher conversion at higher reaction temperatures. Many research groups have also observed similar results (Freedman et al., 1986, Noureddini and Zhu, 1997, and Darnoko and Cheryan, 2000). The reason for this behaviour is due to the endothermic nature of the reaction. The higher reaction temperature would favour endothermic reaction, thus increasing the rate of reaction as well as the ester concentration. However, reaction temperature did not show any significant impact on conversion when using the higher catalyst loading (1.5 wt. %) (See Table 4.8). This is because the reaction was driven close to completion at high catalyst loading.

Results from this part of the study suggest that the higher ester concentration can be obtained at higher reaction temperature. Therefore, the optimum temperature was 50 $^{o}$C. This study suggests that transesterification of FG using solely ethanol can be operated at higher temperatures since ethanol has a higher boiling point (78.4 $^{o}$C).

*4.2.3. Effect of alcohol-to-oil molar ratio*

The effect of alcohol to oil molar ratio (6:1, 9:1, and 12:1) on ester concentration was studied at 30, 40, and 50 $^{o}$C. The results are given in Figures 4.10 - 4.12.

As shown in Figures 4.10, 4.11, and Table 4.8, ester concentration as well as the % conversion decreased as the alcohol-to-oil molar ratio was increased. This can be

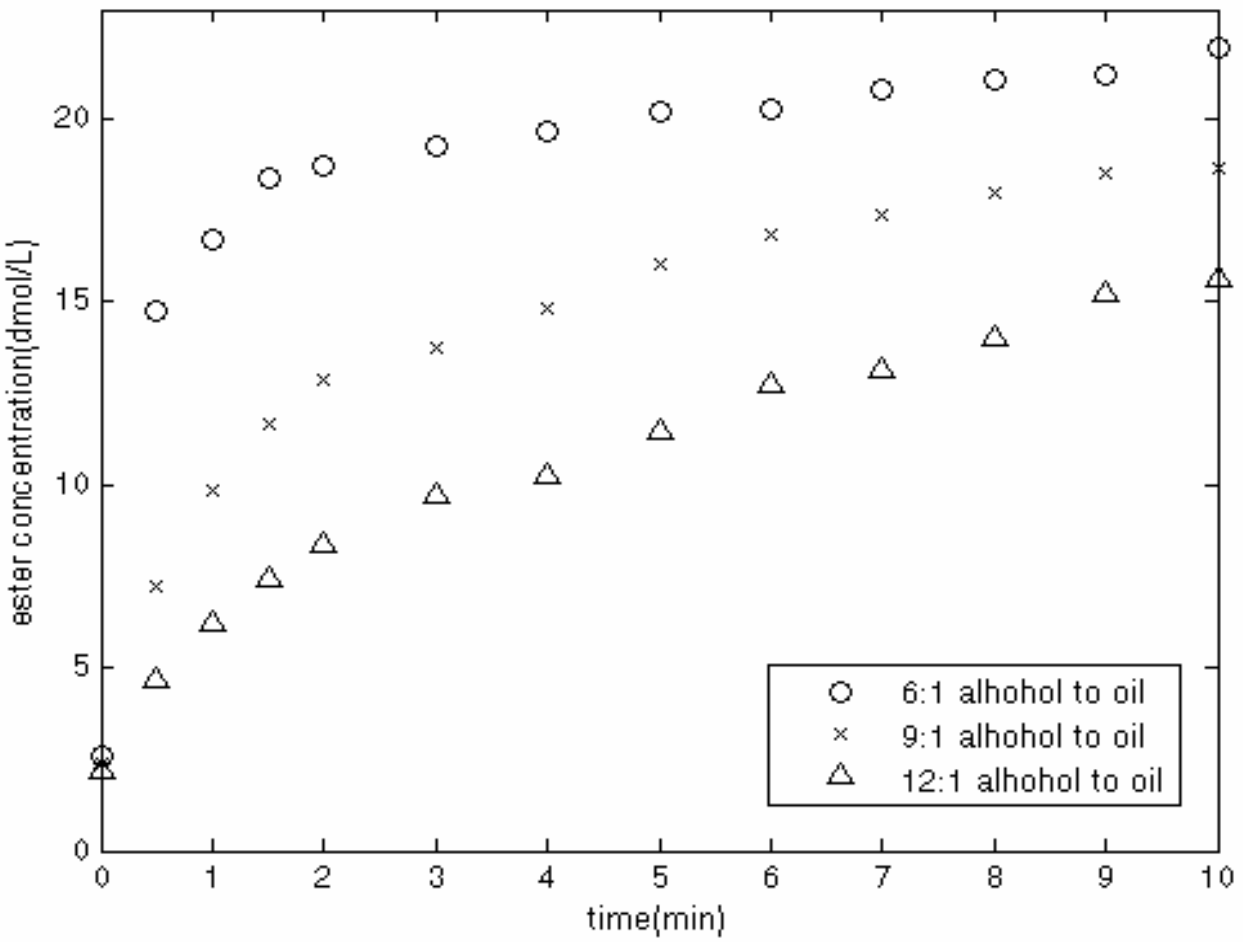



Figure 4.10: Effect of alcohol to oil molar ratio on ester concentration using 1.0 wt. % KOH at 30 $^{o}$C.

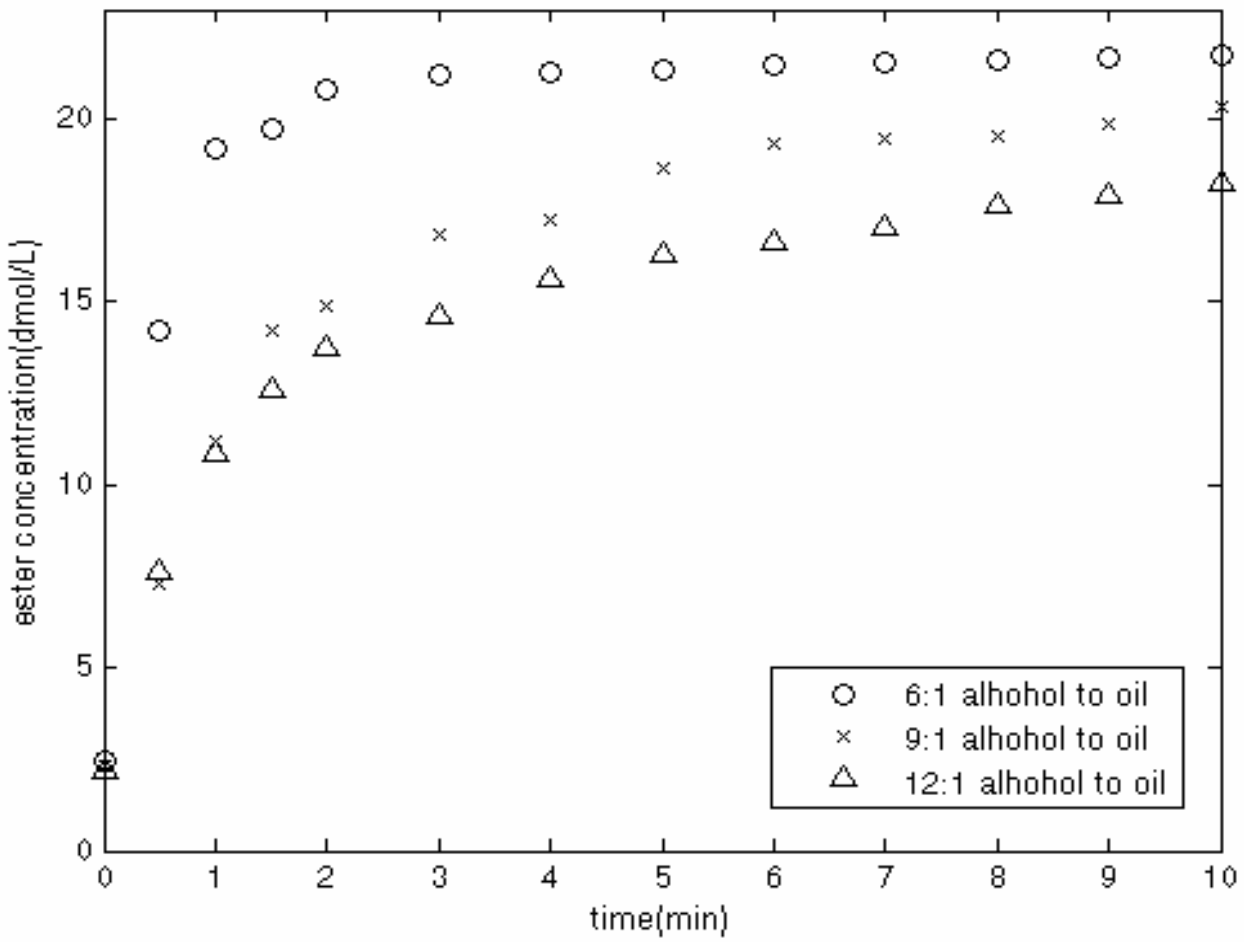



Figure 4.11: Effect of alcohol to oil molar ratio on ester concentration using 1.0 wt. % KOH at 40 $^{o}$C.

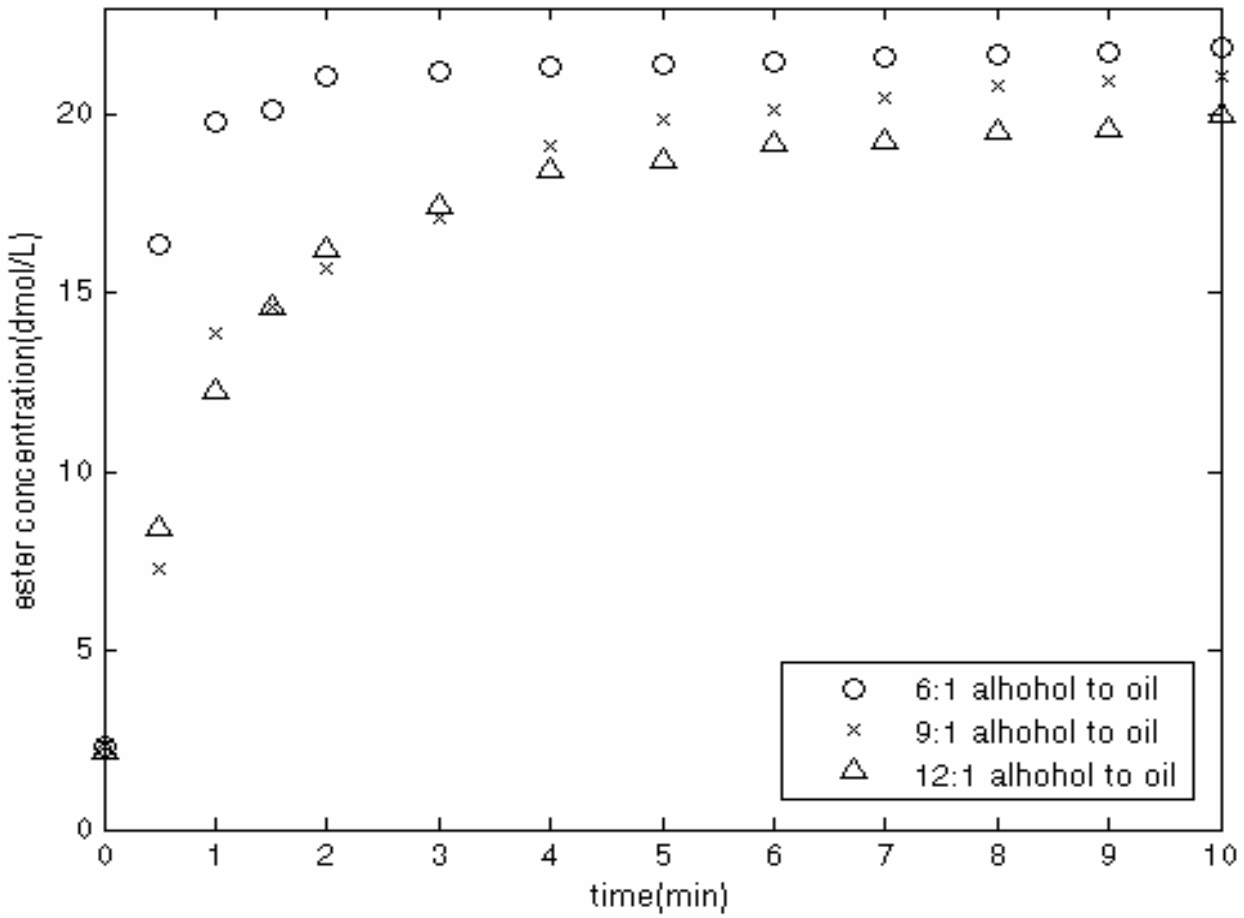



Figure 4.12: Effect of alcohol to oil molar ratio on ester concentration using 1.0 wt. % KOH at 50 $^{o}$C.

explained on the basis of the reactant (oil) concentration in the reaction mixture. By increasing alcohol to oil molar ratio, the amount of alcohol was increased, therefore the FG and catalyst concentrations were diminished, which reduced the rate of reaction. Results published by Boocock et al. (1998) showed a similar trend in which the methyl ester percentage decreased as the alcohol-to-oil molar ratio was increased. In the case of a higher reaction temperature, although the similar trend of ester concentration (ester concentration decreased with an increase in alcohol-to-oil molar ratio) was observed as shown in Figure 4.12, the % conversion increased with alcohol-to-oil molar ratio (See Table 4.8). As alcohol-to-oil molar ratio was increased, the polarity of the system was also increased thus improving ionization of KOH. As a result, the rate of the reaction as well as the % conversion was increased.

Results from this part of the study suggest that the optimum alcohol-to-oil molar ratio operating at low temperature (30 and 40 $^{o}$C) was 6:1. However, the higher alcohol-to-oil molar ratio (12:1) is recommended at higher operating temperature (50 $^{o}$C).

## 4.5. Kinetic study of alkali-catalyzed transesterification of fryer grease

The kinetic study of transesterification of fryer grease was carried out only for the alkali-catalyzed reaction. Before alkali-catalyzed transesterification, the esterification of FFA in FG was carried out in all cases using an acidic catalyst. The detailed procedure for this study was described in Section 3.3.

### *4.5.1. Alkali-catalyzed transesterification analysis*

Alkali-catalyzed transesterification of FG was studied at three reaction temperatures (30, 40, and 50$^{o}$C), three alcohol to oil molar ratios (6:1, 9:1, and 12:1), and

two catalyst loadings (0.5 and 1.0 wt. % KOH). The transesterification reaction is a stepwise reaction consisting of a number of consecutive, reversible reactions as shown below:

$$TG + AL \xrightarrow{k1} DG + ES \quad \ldots (4.1)$$

$$DG + ES \xrightarrow{k2} TG + AL \quad \ldots (4.2)$$

$$DG + AL \xrightarrow{k3} MG + ES \quad \ldots (4.3)$$

$$MG + ES \xrightarrow{k4} DG + AL \quad \ldots (4.4)$$

$$MG + AL \xrightarrow{k5} GL + ES \quad \ldots (4.5)$$

$$GL + ES \xrightarrow{k6} MG + AL \quad \ldots (4.6).$$

Here TG = Triglycerides; DG = Diglycerides; MG = Monoglycerides; GL = Glycerol; AL = Alcohol; and ES = Ester.

Typical concentration profiles of triglyceride (TG), diglyceride (DG), monoglyceride (MG), methyl ester (ES), and glycerol (GL) for alkali-catalyzed transesterification of fryer grease, with methanol to oil molar ratio of 6:1 at 40 $^{o}$C using 0.5% KOH, are shown in Figure 4.13. This figure indicates the rate of conversion of triglycerides and formation of esters and glycerol as well as the intermediate compounds such as diglycerides and monoglycerides (See Equation (4.1)-(4.6)).

Rapid changes in the concentration of each component were observed in the initial period of the reaction. This indicates that the crucial period for alkali-catalyzed transesterification of fryer grease was the first 5 min of the reaction. After 5 min, no significant changes in the concentration of each component were observed. There are two explanations for this phenomenon. First, the change in concentrations drops as the reaction approaches equilibrium. Second, methyl ester and glycerol are immiscible with

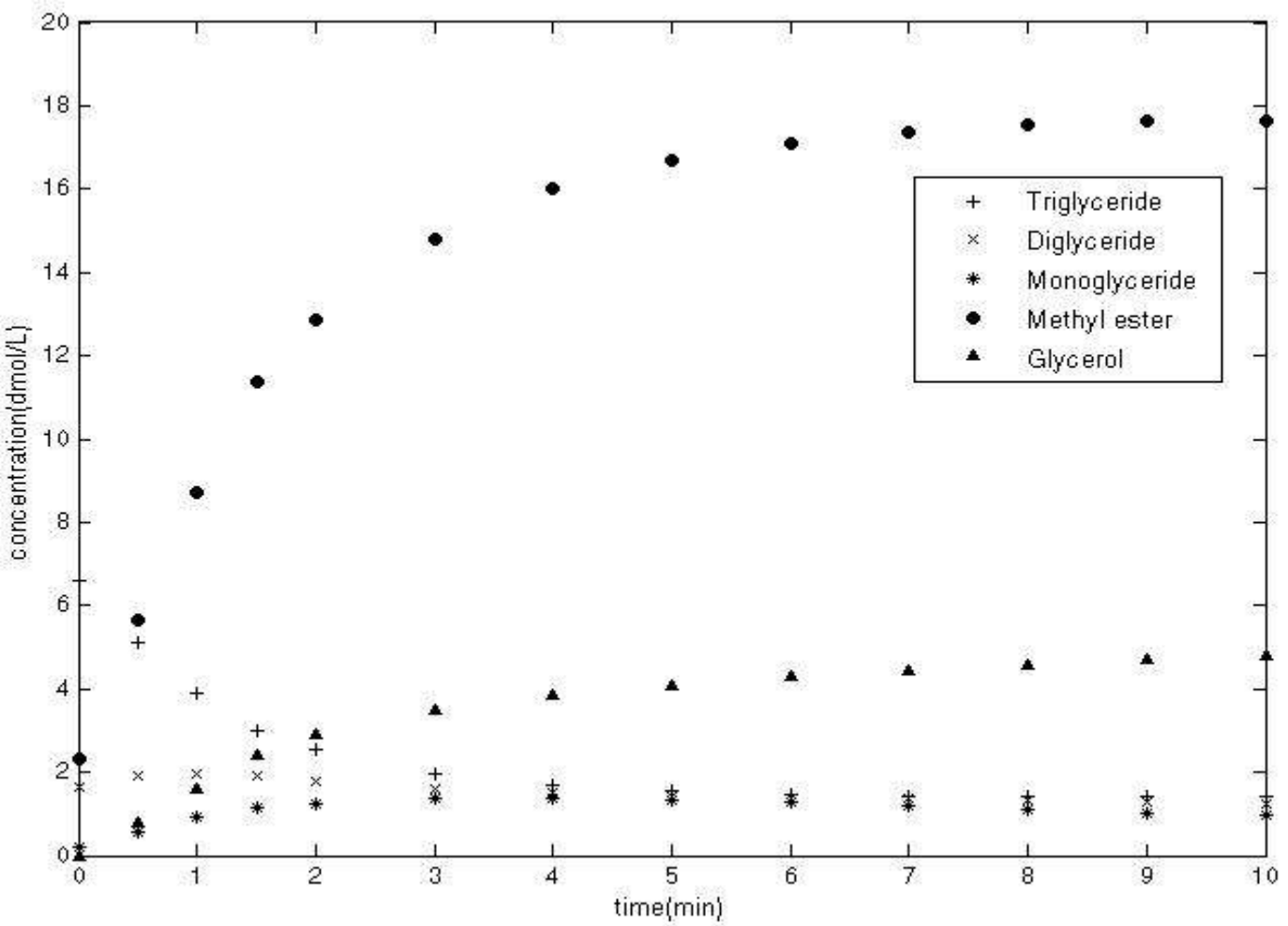



Figure 4.13: Concentration profile during transesterification of fryer grease with 6:1 methanol to oil molar ratio using 0.5 wt. % KOH at 40 $^{o}$C and at a stirring speed of 600 rpm.

each other even at a higher stirring speed of 600 rpm (Vicente et al., 2005). Also, the glycerol-rich phase is formed as the reaction proceeds even in the presence of a cosolvent (Zhou et al., 2003). Once glycerol forms, the catalyst is transferred into a glycerol phase, thus lowering the catalyst concentration in the ester phase thereby lowering the reaction rate. Similar trends in concentration profiles were observed in each experiment (See Appendix F).

In 1986, Freedman et al. conducted an experiment on methanolysis of soybean oil using an alkaline catalyst. They reported an S-shaped result of the ester formation curve (See Figure 2.6). Boocock et al. (1996) explained that the lag time at the initial stage of the reaction was due to mass transfer limitation. They explained that the solubility of oil in methanol is low, hence it takes a significant amount of time for oil to reach saturation level in the methanol phase. Vicente et al. (2005) carried out methanolysis of sunflower oil using KOH as a catalyst. They concluded that at a stirring speed of 600 rpm, the region of mass transfer control can be neglected. A recent study also stresses the importance of a high stirring speed of 600 rpm as a crucial factor for the transesterification reaction (Meher et al., 2005).

In this study, stirring speed was fixed at 600 rpm in order to minimize the mass transfer effect. As a result, lag time at the initial stage of the reaction was not observed (See Figure 4.13). The data is also reported in Appendix F.

*4.5.2. Determining rate determining step (RDS) of alkali-catalyzed transesterification of fryer grease*

The effective rate constants (k') were defined for forward reactions (See appendix C) and were calculated based on the experimental data for the period of the first 5 min. of

the reaction. The equations used to calculate the effective rate constants of the reactions were derived under the assumption that the forward and backward reactions follow first and second order overall kinetics, respectively (See Appendix C). The effective rate constants calculated for transesterification of fryer grease with 6:1 methanol to oil molar ratio using 0.5% KOH are shown in Table 4.9. To determine the accuracy of the calculated effective rate constants, experimental values vs. calculated data of tri-, di-, and monoglycerides are compared as shown in Figures 4.14, 4.15, and 4.16, respectively. The correlation coefficient for the data in Figures 4.14, 4.15, and 4.16 are 0.9998, 0.9886, and 0.9814, respectively, indicating that the data predicted using calculated k values are accurate. Figure 4.17 shows plots of tri-, di-, and monoglyceride concentration profiles with time obtained experimentally (dots) and mathematically (solid lines) from equations (C19), (C28), and (C37).

Since the reaction order and hence the units of k for forward and backward reactions are not the same, a direct comparison of forward and backward rate constants cannot be made. The effective rate constant for the triglyceride conversion is the lowest of all the effective rate constants for forward reactions at all reaction temperatures (See Table 4.9). This indicates that the rate determining step (RDS) for overall alkali-catalyzed transesterification of fryer grease was the first step, i.e., conversion of triglyceride to diglyceride.

The effective rate constants for the RDS of an alkali-catalyzed transesterification using 1 % KOH and 6:1, 9:1, and 12:1 alcohol to oil molar ratios at different temperatures are presented in Table 4.10. The effective rate constants of the RDS of transesterification of FG were increased from 0.3346 to 2.5197 $min^{-1}$, from 0.6149 to

Table 4.9. The rate constants of transesterification of fryer grease using 6:1 alcohol to oil molar ratio and 0.5 wt. % KOH at various temperatures

| Reaction | Rate constant [unit] | Temperature | | |
|---|---|---|---|---|
| | | 30 °C | 40 °C | 50 °C |
| TG → DG | $k'_1$ [$min^{-1}$] | 0.3346 | 0.6149 | 0.8333 |
| DG → TG | $k_2$ [$L \cdot dmol^{-1} \cdot min^{-1}$] | 0.0352 | 0.0412 | 0.0534 |
| DG → MG | $k'_3$ [$min^{-1}$] | 0.7576 | 1.3666 | 1.7754 |
| MG → DG | $k_4$ [$L \cdot dmol^{-1} \cdot min^{-1}$] | 0.0914 | 0.0946 | 0.1163 |
| MG → GL | $k'_5$ [$min^{-1}$] | 1.7490 | 2.6302 | 2.0483 |
| GL → MG | $k_6$ [$L \cdot dmol^{-1} \cdot min^{-1}$] | 0.0673 | 0.0613 | 0.0387 |

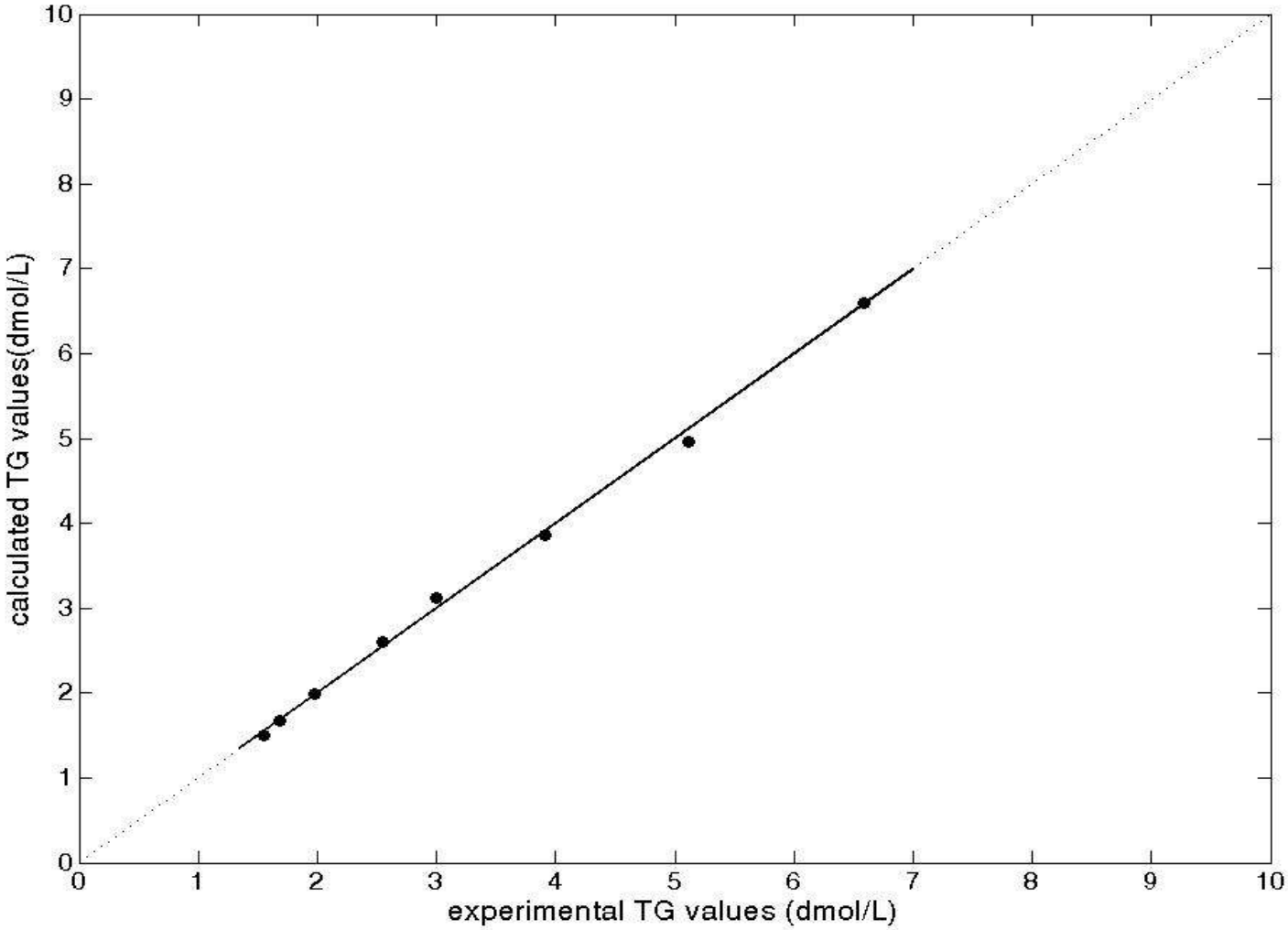



Figure 4.14: Calculated triglyceride concentration vs. experimental triglyceride concentration using 6:1 alcohol to oil molar ratio, 0.5 wt. % KOH at 40 $^{o}$C.

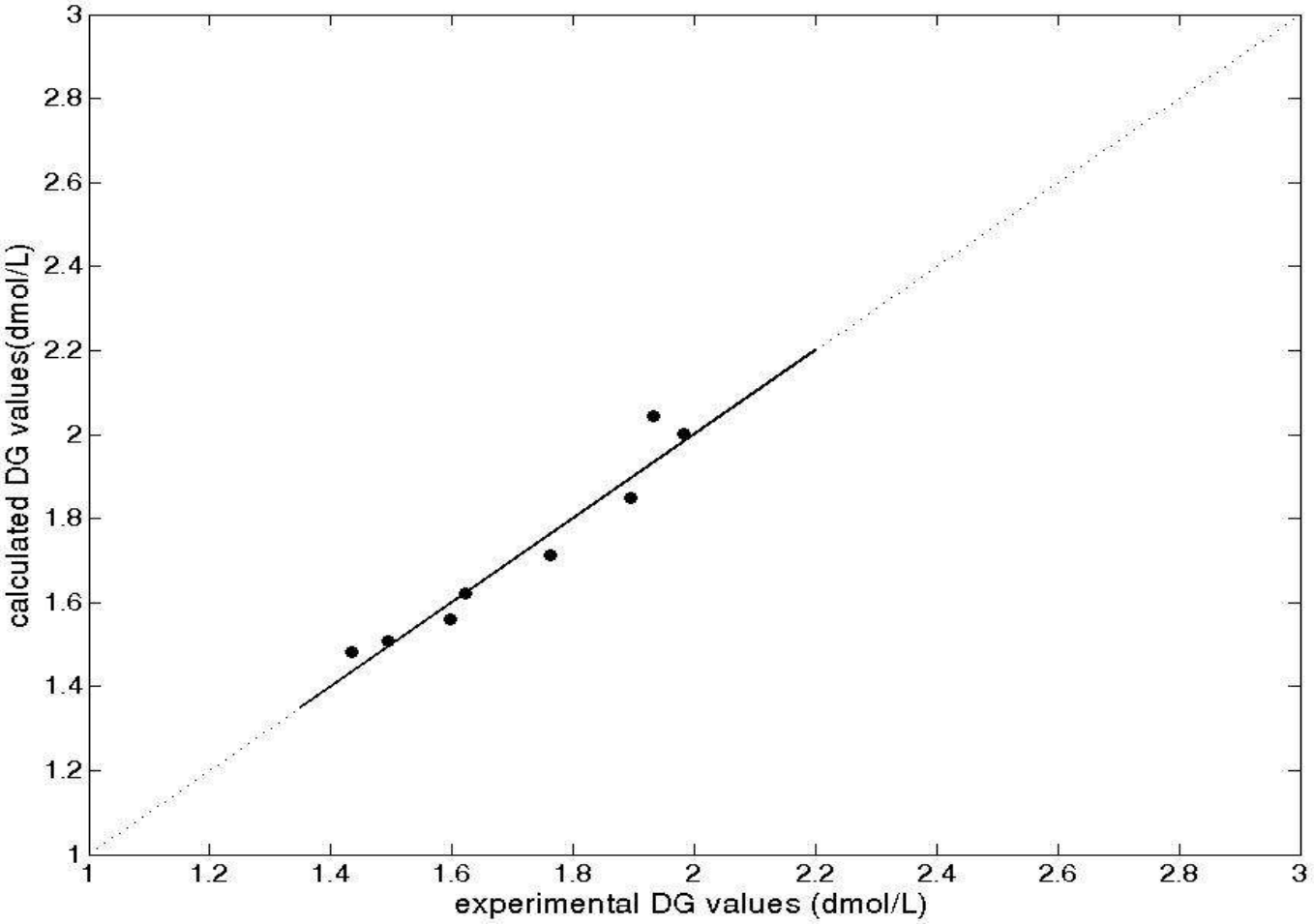



Figure 4.15: Calculated diglyceride concentration vs. experimental diglyceride concentration using 6:1 alcohol to oil molar ratio, 0.5 wt. % KOH at 40 $^{o}$C.

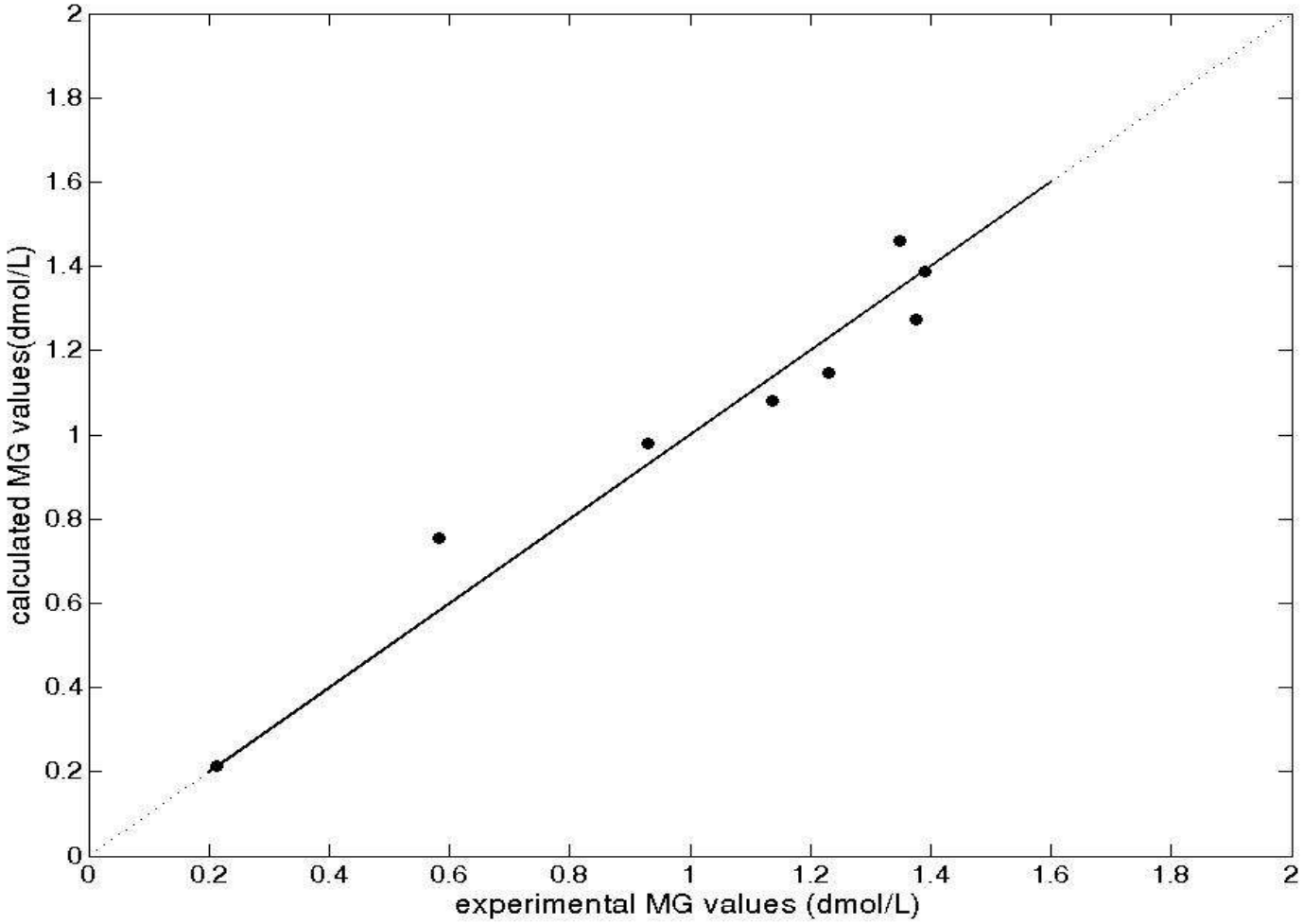



Figure 4.16: Calculated monoglyceride concentration vs. experimental monoglyceride concentration using 6:1 alcohol to oil molar ratio, 0.5 wt. % KOH at 40 $^{o}$C.

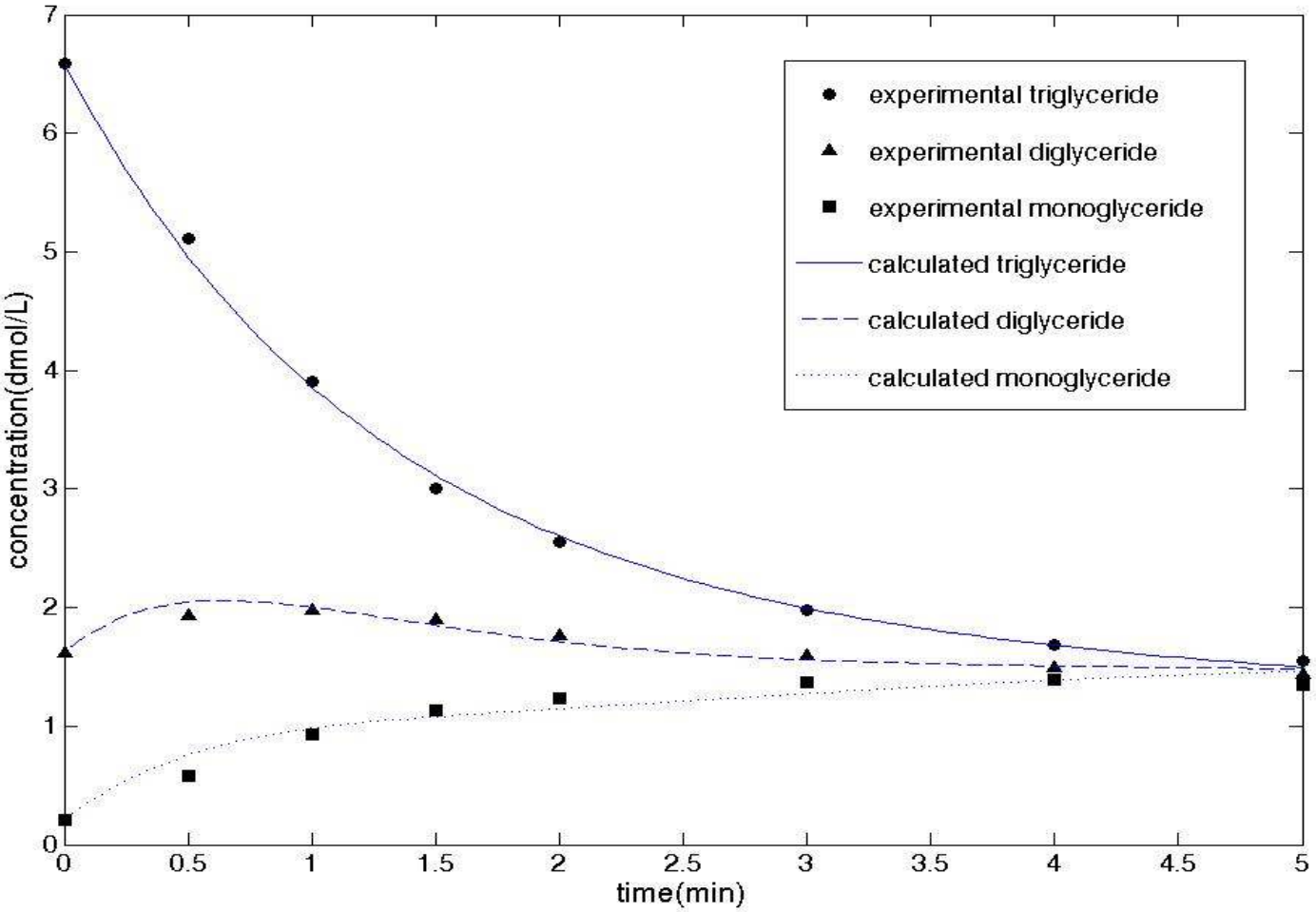



Figure 4.17: Calculated and experimental results of tri-, di-, and monoglyceride concentration vs. time using 6:1 alcohol to oil molar ratio, 0.5 wt. % KOH at 40 $^{o}$C.

Table 4.10. The rate constants of transesterification of fryer grease using 1.0 wt. % KOH at various alcohol to oil molar ratio and temperatures

| Alcohol to oil molar ratio | Reaction | Rate constant [unit] | Temperature | | |
|---|---|---|---|---|---|
| | | | 30 °C | 40 °C | 50 °C |
| 6:1 | TG → DG | $k'_1$ [$min^{-1}$] | 2.5197 | 3.1477 | 3.7500 |
| | DG → TG | $k_2$ [$L \cdot dmol^{-1} \cdot min^{-1}$] | 0.1232 | 0.1052 | 0.1412 |
| 9:1 | TG → DG | $k'_1$ [$min^{-1}$] | 0.9567 | 0.9985 | 1.1559 |
| | DG → TG | $k_2$ [$L \cdot dmol^{-1} \cdot min^{-1}$] | 0.0855 | 0.0529 | 0.0518 |
| 12:1 | TG → DG | $k'_1$ [$min^{-1}$] | 0.4787 | n/a | n/a |
| | DG → TG | $k_2$ [$L \cdot dmol^{-1} \cdot min^{-1}$] | 0.0745 | n/a | n/a |

3.1477 $min^{-1}$, and from 0.8333 to 3.7500 $min^{-1}$ when catalyst loading was increased from 0.5 to 1.0 wt. % at 30, 40, and 50 $^{o}C$ respectively. These results suggest that the reaction occurred faster at higher catalyst loadings. Also, the effective rate constants of the RDS of fryer grease transesterification corresponding to Figure 4.8 increased from 0.3346 to 0.6149 to 0.8333 $min^{-1}$ when the reaction temperature was increased from 30 to 40 to 50 $^{o}C$, respectively. This indicates that the RDS of transesterification of FG is favored at higher temperatures. This is a typical observation for an endothermic reaction. Considering a reaction temperature of 30 $^{o}C$, the effective rate constants decreased as the alcohol to oil molar ratio was increased indicating that the reaction rates are slower at higher alcohol to oil ratios due to the higher extent of dilution of the oil at higher molar concentrations.

*4.5.3. The activation energy*

The activation energy determines the extent of dependency of rate constants on reaction temperature at a given condition. The activation energies of the RDS (Conversion of triglyceride to diglyceride) at different catalyst loadings of 0.5 and 1.0 wt. % were calculated based on the Arrhenius equation (Equation (3.4)). Arrhenius plots for RDS are presented in Figures 4.18 and 4.19 for the transesterification of fryer grease at three different temperatures (30, 40, and 50 $^{o}C$) using 0.5 and 1.0 wt. % KOH and 6:1 alcohol to oil molar ratio, respectively. Figure 4.20 shows Arrhenius plot for the backward of RDS when 0.5 % KOH and 6:1 alcohol to oil molar ratio was used. The correlation coefficients for Arrhenius plot of the RDS of transesterification of FG in all these cases exceeds 0.95. Table 4.11 shows activation energy and the corresponding

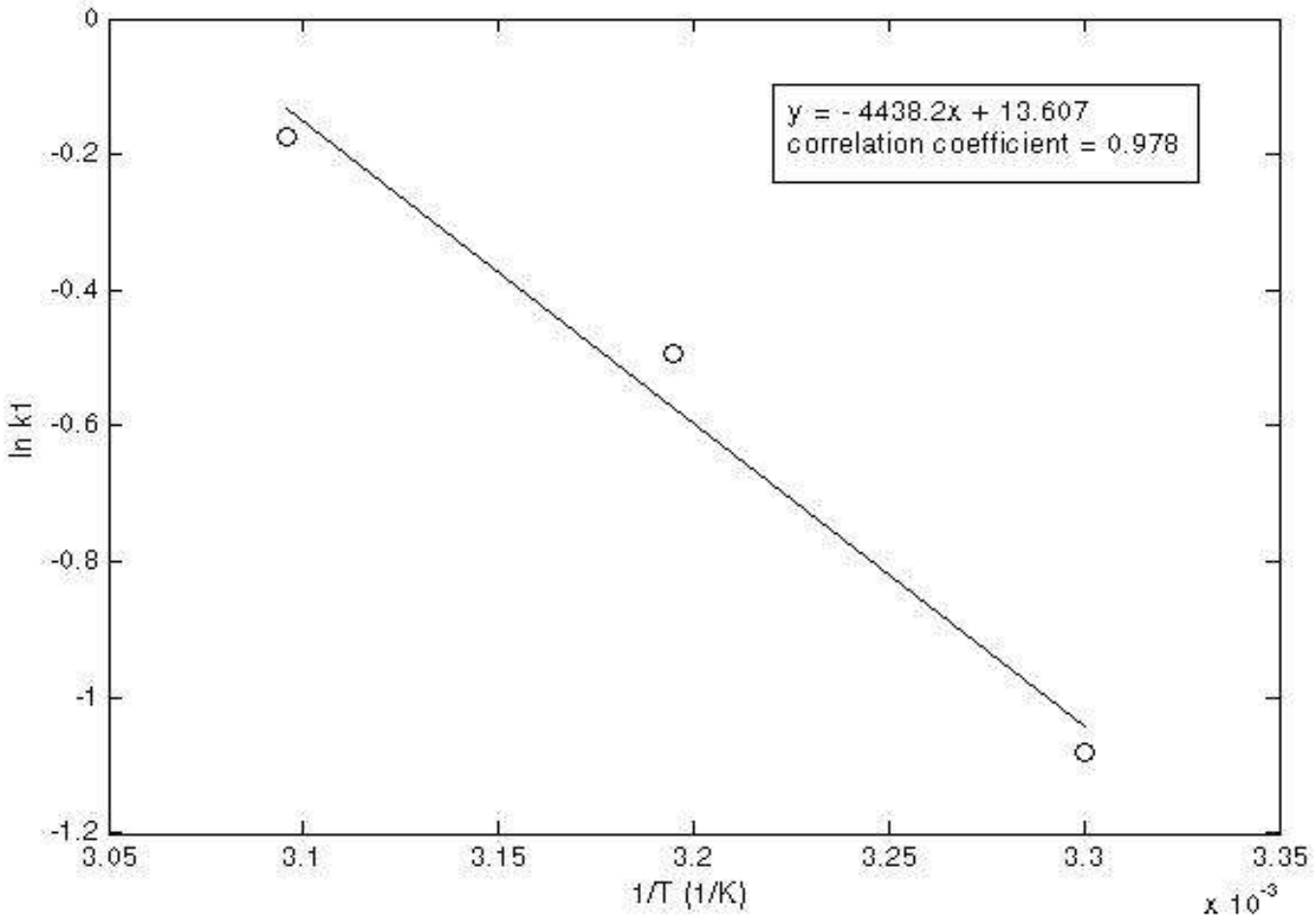



Figure 4.18: Arrhenius plot for rate determining step of transesterification of fryer grease at 6:1 alcohol to oil molar ratio and 0.5 wt. % KOH.

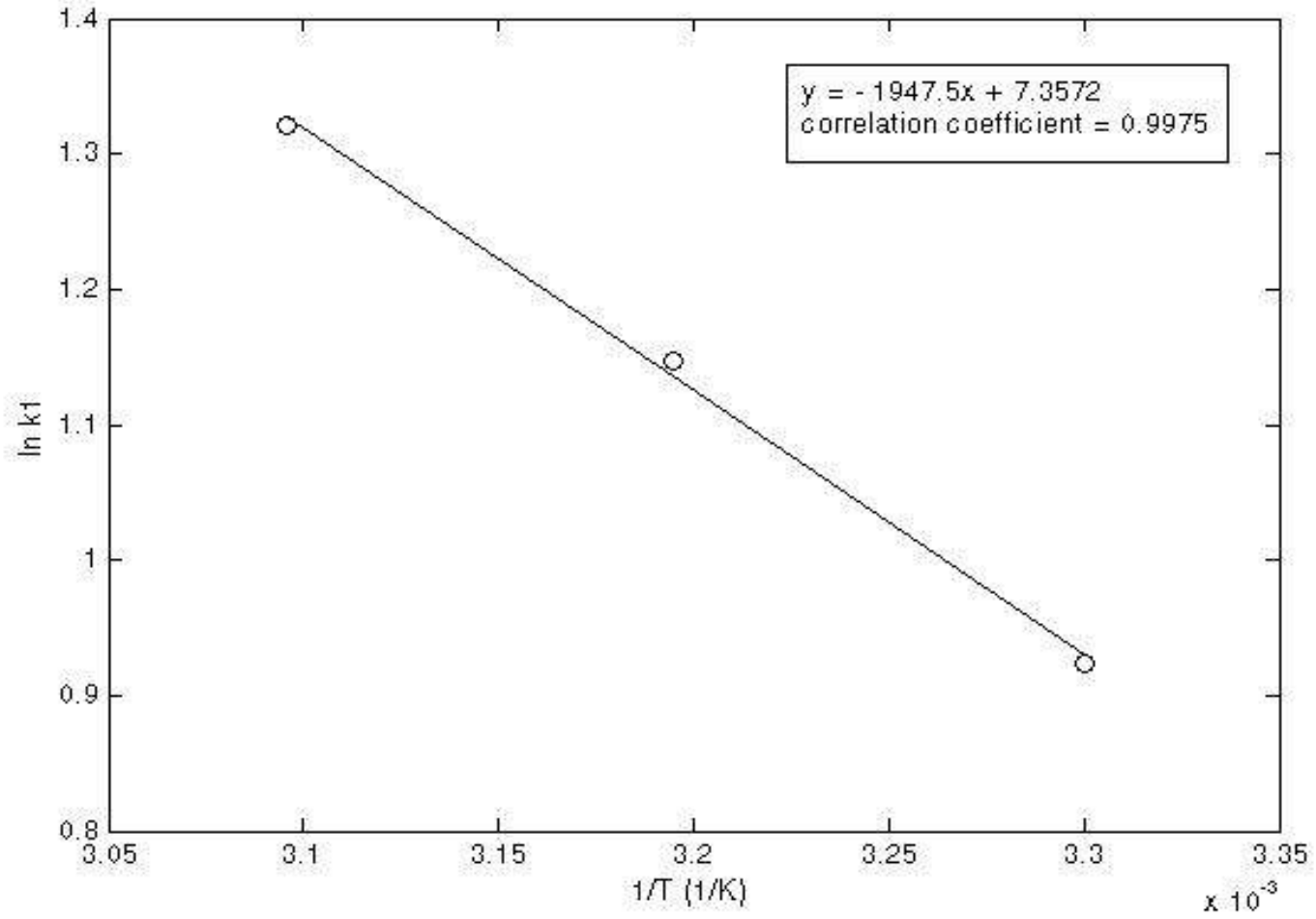



Figure 4.19: Arrhenius plot of rate determining step of transesterification of fryer grease at 6:1 alcohol to oil molar ratio and 1.0 wt. % KOH.

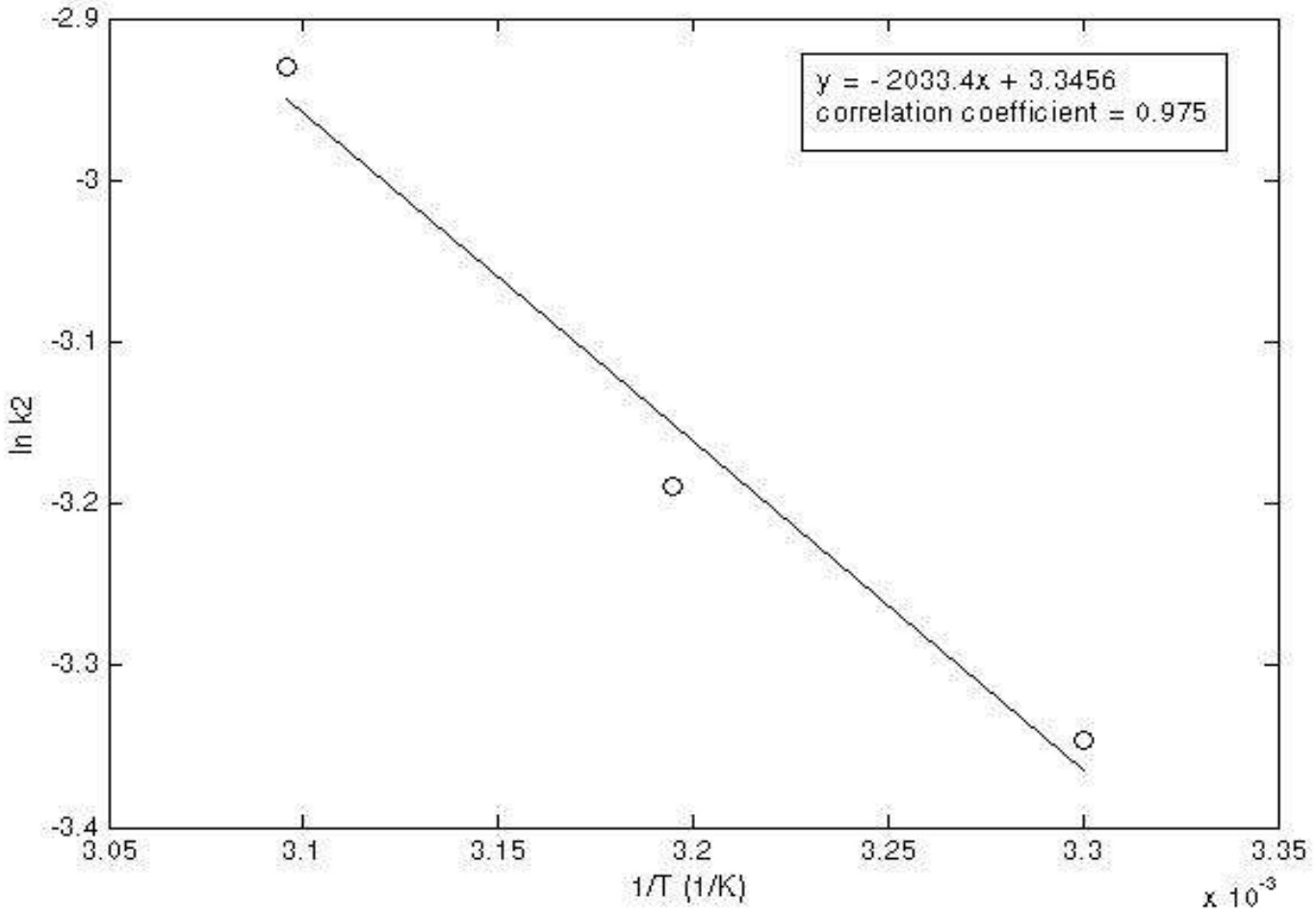



Figure 4.20: Arrhenius plot of backward reaction of rate determining step of transesterification of fryer grease at 6:1 alcohol to oil molar ratio and 0.5 wt. % KOH.

Table 4.11. Activation energy of alkali-catalyzed transesterification of fryer grease at different conditions

| Reaction | Catalyst concentration | Alcohol to oil molar ratio | Activation energy [kJ·mol$^{-1}$] | Correlation coefficients |
|---|---|---|---|---|
| TG → DG | 0.5 wt. % | 6:1 | 36.9 | 0.978 |
| | 1.0 wt. % | 6:1 | 16.2 | 0.998 |
| DG → TG | 0.5 wt. % | 6:1 | 16.9 | 0.975 |

correlation coefficients of the RDS and its backward reaction of transesterification of fryer grease.

Activation energies in this study ranged from 16.2 to 36.9 kJ/mol (See Table 4.11). Vicente et al. (2005) reported an activation energy of 31.7 kJ/mol for the reaction involving the conversion of triglyceride to diglyceride during the methanolysis of sunflower oil, which falls in the range of this study. Activation energy shows how strong the rate of reaction depends on reaction temperature. In this study, the activation energy decreased when the catalyst loading was increased. This indicates that the reactions operated at higher catalyst concentrations were not very sensitive to reaction temperature. When catalyst concentration was increased from 0.5 to 1.0 wt. %, activation energy of RDS of FG transesterification decreased from 37 to16 kJ/mol, thus it was easier to initiate the reaction when a higher catalyst concentration was used. Activation energy of the backward reaction is somewhat lower than that of the forward one. This indicates that the product diglyceride is less stable and has higher potential energy than the reactant triglyceride. In this type of reaction, heat is absorbed from the surroundings in the reactant mixture. Therefore, it can be concluded that the RDS of fryer grease methanolysis using KOH as a catalyst was an endothermic reaction (Chang, 2006).

# 5. CONCLUSIONS AND RECOMMENDATIONS

## 5.1. Conclusions

1. The ester yield obtained from the two-step transesterification process ranged from 60 to 91 wt. %. The yield of biodiesel varies with the quality of the feed stock. It can be improved if a feedstock with more purity (higher concentration of triglyceride) is used.
2. Transesterification with mixed alcohols gave higher yields than those with a single alcohol. This is because the higher reactivity of methanol drove the reaction close to equilibrium while the better solubility of ethanol reduced the mass transfer resistance.
3. When mixed methyl-ethyl alcohol was used in the transesterification process, ethyl ester was also formed, in a lesser amount, along with methyl ester. Oleic acid was found to be the dominant fatty acid in esters derived from fryer grease.
4. Esters obtained from the two-step transesterification of fryer grease possess properties that meet ASTM standards D-6751. When 1 vol. % of FG esters was added to kerosene, its lubricity was enhanced by up to 33%.
5. In this study, the rate of formation of ester can be increased by increasing reaction temperature, catalyst concentration, or decreasing alcohol to oil molar ratio. The optimum conditions for fryer grease methanolysis are a reaction temperature of 50 $^{o}$C and 1.0 wt% KOH. The 6:1 alcohol-to-oil molar ratio was found to be optimum at low reaction temperatures (30 and 40 $^{o}$C). At high reaction temperature (50 $^{o}$C), 12:1 alcohol-to-oil molar ratio is recommended.

6. The first 5 min of alkali-catalyzed transesterification of fryer grease was the crucial period of the reaction where rapid changes in the concentration of each component occurred.
7. Conversion of triglyceride to diglyceride was found to be the rate determining step of the overall reaction.
8. The activation energy was reduced with an increase in catalyst loading. This result indicates that the reaction was easier to initiate when more catalyst was used. The rate determining step of alkali-catalyzed transesterification was found to be an endothermic reaction.

## 5.2. Recommendations

1. The addition of fresh vegetable oil to fryer grease should help to improve ester yield and quality. The study on the effect of the addition of fresh vegetable oil to fryer grease on ester yield and properties is recommended.
2. Emission testing should be performed when esters derived from fresh vegetable oil, fryer grease, and mixtures of fresh vegetable oil and fryer grease are used in a diesel engine.
3. The cost of the ester purification process may be reduced if a heterogeneous catalyst is used instead of a homogeneous catalyst, mostly because of the easy separation of ester and glycerol from the catalyst. Synthesis, characterization, and regeneration of the heterogeneous catalyst used in transesterification of vegetable oil are recommended.

4. The storage stability is another important property of biodiesel. Study on storage stability of biodiesel derived from fryer grease is recommended.
5. A pilot plant study for transesterification of fryer grease should be performed.

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# APPENDICES

## Appendix A: Standards for biodiesel specifications

Table A1. ASTM D-6751-03a standard for biodiesel (B100)

| Property | Limits | Units |
|---|---|---|
| Flash point (closed cup) | 130.0 min | $^{o}C$ |
| Water and sediment | 0.050 max | % volume |
| Kinematic viscosity, 40$^{o}$C | 1.9 – 6.0 | $mm^2/s$ |
| Sulfated ash | 0.020 max | % mass |
| Sulfur | 0.0015 max | % mass |
| Copper strip corrosion | No. 3 max | |
| Cetane number | 47 min | |
| Carbon residue | 0.050 max | % mass |
| Acid number | 0.80 max | mg KOH/g |
| Free glycerine | 0.020 | % mass |
| Total glycerine | 0.240 | % mass |
| Phosphorus content | 0.001 max | % mass |
| Distillation temperature, 90 % recovered | 360 max | $^{o}C$ |

Table A2. PR EN 14214 standard for biodiesel (B100)

| Property | Limits | Units |
|---|---|---|
| Flash point | 101 min | $^{o}C$ |
| Oxidative stability, 110 $^{o}C$ | 6.0 min | hours |
| Linolenic acid methyl ester | 12 max | % (m/m) |
| Polyunsaturated (>= 4 double bonds) methyl esters | 1.0 max | % (m/m) |
| Water content | 500 max | mg/kg |
| Total contamination | 24 max | mg/kg |
| Kinematic viscosity, 40$^{o}C$ | 3.5 - 5.0 | $mm^2/s$ |
| Density, 15$^{o}C$ | 860 - 900 | $kg/m^3$ |
| Sulfur content | 10 max | Mg/kg |
| Copper strip corrosion (3 hr at 50 $^{o}C$) | Class 1 | rating |
| Carbon residue (on 10 % distillation residue) | 0.3 max | % (m/m) |
| Acid value | 0.50 max | Mg KOH/g |
| Iodine value | 120 max | |
| Methanol content | 0.2 max | % (m/m) |
| Monoglyceride content | 0.8 maz | % (m/m) |
| Diglyceride content | 0.2 max | % (m/m) |
| Triglyceride content | 0.1 max | % (m/m) |
| Free glycerine | 0.02 | % (m/m) |
| Total glycerine | 0.25 | % (m/m) |
| Alkaline metals (Na + K) | 5.0 max | mg/kg |
| Phosphorus content | 10 max | mg/kg |

## Appendix B: Sample calculation

## Alcohol needed for esterification of FFA and transesterification of FG

Oil 1 mole needs alcohol of 6 moles + alcohol for esterification of FFA

50 g of oil has ~2.5 g of FFA ~2.5/282 = 0.0088 mole

50 g of oil has ~50/884 = 0.05656 mole

Each step needs alcohol, 0.05656*3 = 0.1697 mole

For methanol:

*First step:*

MeOH required = (0.1697+0.0088)*32 = 5.71 g

*Second step:*

MeOH required = 0.1697*32 = 5.42 g

For ethanol:

*First step:*

EtOH required = (0.1697+0.0088)*46 = 8.21 g

*Second step:*

EtOH required = 0.1697*46 = 7.81 g

## KOH needed to neutralized $H_2SO_4$

$$H_2SO_4 + 2KOH \rightarrow K_2SO_4 + 2H_2O \quad \ldots \text{(B1)}$$

1 mole $H_2SO_4$ needs 2 mole KOH

98.08 g of $H_2SO_4$ needs 112.22 g KOH

1 g of $H_2SO_4$ needs 1.144 g KOH

## Unit conversion from wt% obtained from HPLC to mol/L

From fatty acid composition;

Average MW of fatty acid = $\frac{\sum x_i \times MW_i}{\sum x_i} \cong 279.6$

Where;

$x_i$ = Mole fraction of component i contained in fryer grease

$MW_i$ = Molecular weight of component i

MW of TG = (278.6)*3 + 14 + 13 + 14 = 876.8

MW of DG = (278.6)*2 + 14 + 13 + 14 + 17 = 615.2

MW of MG = 278.6 + 14 + 13 + 14 + 17 + 17 = 353.6

MW of GL = 14 + 13 + 14 + 17 +17 +17 = 92

MW of ES (methyl) = 278.6 + 15 = 293.6

Density of FG = 0.94 g/mL

Density of MeOH = 0.79 g/mL

Total reactant volume

From saponification value of fryer grease batch 2;

MW of FG = 946.19

*At 6:1 MeOH : FG molar ratio;*

FG 100 g need MeOH 20.29 g = 0.0257 L

FG 100 g = 0.107 L

Total reactant volume = 0.0257 + 0.107 = 0.1327 L

*At 9:1 MeOH : FG molar ratio;*

FG 100 g needs MeOH 30.44 g = 0.0386 L

FG 100 g = 0.107 L

Total reactant volume = 0.0386 + 0.107 = 0.1456 L

*At 12:1 MeOH : FG molar ratio;*

FG 100 g needs MeOH 40.5836 g = 0.0514 L

FG 100 g = 0.107 L

Total reactant volume = 0.0514 + 0.107 = 0.1584 L

Example Data point at 1 min. of alkali-catalyzed transesterification of FG with 6:1 MeOH : FG molar ratio at 40 $^{o}$C using 0.5 %KOH

| Component | Percentage |
|---|---|
| TG | 45.5 |
| DG | 16.2 |
| MG | 4.4 |
| ES | 33.9 |

Consider TG;

45.5 g of TG in 100 g of TG+DG+MG+ES ~ 100 g of FG

100 g of FG has total reactant volume = 0.1327 L

$$45.5\ \%\ \text{TG} = 45.5g \times \frac{mole}{876.8g} \times \frac{1}{0.1327L} = 0.39\ mole/L$$

Similarly,

16.2 % DG = 0.20 mole/L

4.4 % MG = 0.09 mole/L

33.9 % ES = 0.87 mole/L

## Calculation of glycerol concentration

Glycerol concentration can be calculated based on the assumption that number of moles of glycerol group remains unchanged during transesterification, therefore

$$n_{TG0} + n_{DG0} + n_{MG0} = n_{TGi} + n_{DGi} + n_{MGi} + n_{GLi} \quad \ldots \text{(B2)}$$

Where;

$n_{TG0}$ = Number of moles of triglyceride at initial stage (t=0)
$n_{TDG0}$ = Number of moles of diglyceride at initial stage (t=0)
$n_{TMG0}$ = Number of moles of monoglyceride at initial stage (t=0)
$n_{TGi}$ = Number of moles of triglyceride at time t=ti
$n_{DGi}$ = Number of moles of diglyceride at time t=ti
$n_{MGi}$ = Number of moles of monoglyceride at time t=ti
$n_{GLi}$ = Number of moles of glycerol at initial time t=ti

## Calculation of conversion for process optimization study

$$conversion = \frac{mol\ acyl\ group\ converted}{initial\ mol\ of\ acyl\ group} = \frac{mol\ ester\ produced}{initial\ mol\ of\ acyl\ group} \quad \ldots \text{(B3)}$$

$$conversion = \frac{n_{ESi} - n_{ES0}}{\left(3n_{TG0} + 2n_{DG0} + n_{MG0}\right)} \quad \ldots \text{(B4)}$$

Where;

$n_{TG0}$ = Number of moles of triglyceride at initial stage (t=0)
$n_{TDG0}$ = Number of moles of diglyceride at initial stage (t=0)
$n_{TMG0}$ = Number of moles of monoglyceride at initial stage (t=0)
$n_{ES0}$ = Number of moles of ester at initial stage (t=0)
$n_{ESi}$ = Number of moles of ester at time t=ti

## Appendix C: Rate expression derivation

Transesterification reactions:

$$TG + AL \xrightarrow{k1} DG + ES \quad \ldots (C1)$$

$$DG + ES \xrightarrow{k2} TG + AL \quad \ldots (C2)$$

$$DG + AL \xrightarrow{k3} MG + ES \quad \ldots (C3)$$

$$MG + ES \xrightarrow{k4} DG + AL \quad \ldots (C4)$$

$$MG + AL \xrightarrow{k5} GL + ES \quad \ldots (C5)$$

$$GL + ES \xrightarrow{k6} MG + AL \quad \ldots (C6)$$

Where;

TG = Triglycerides

DG = Diglycerides

MG = Monoglycerides

GL = Glycerol

AL = Alcohol

ES = Ester

*Assumption:* the rate equations follow first order reaction with respect to each component involved in the corresponding reaction.

Determination of $k_1$ and $k_2$

Rate of concentration change of TG is rate of formation of TG in (C2), subtract rate of disappearance of TG in (C1):

$$\frac{dC_T}{dt} = r_T = r_{1T} + r_{2T} = -k_1 C_T C_A + k_2 C_D C_E$$

where $C_T$, $C_A$, $C_D$, and $C_E$ are concentration of triglyceride, alcohol, diglyceride and ester respectively. Since alcohol concentration used in the reaction was in excess, it can be considered as a constant. Then we define, effective rate constant, $k'_1 = k_1 C_A$.

$$\frac{dC_T}{dt} = r_T = r_{1T} + r_{2T} = -k'_1 C_T + k_2 C_D C_E \quad \ldots (C7)$$

In order to find a solution to equation (C7), we need to express $C_D$ and $C_E$ as a function of time.

*Development of function $C_D$*

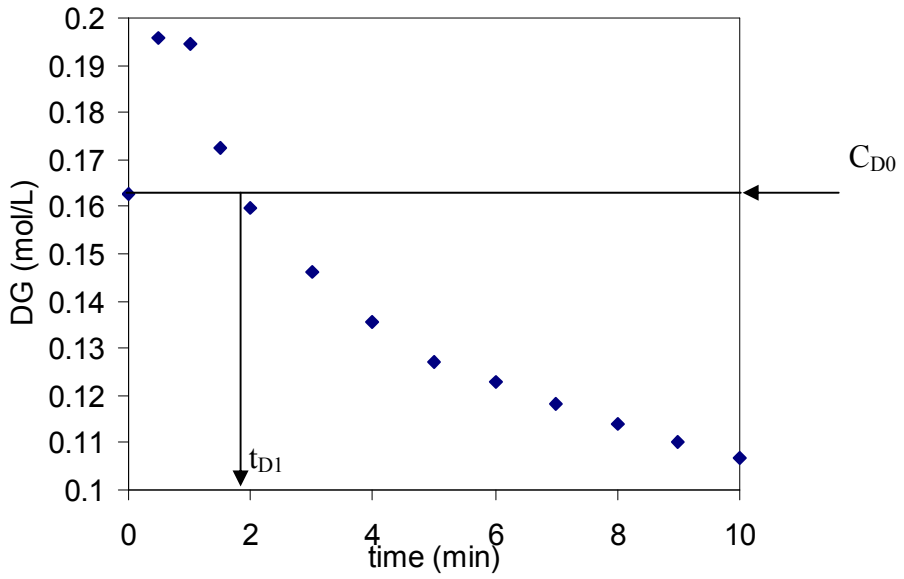


Figure C1: Typical diglyceride concentration profile.

At the initial period (time t=o to $t=t_{D1}$), diglyceride concentration was increased and then decreased. The suggested formula for this type of change in concentration is composed of two exponential terms [Fogler, 1999]:

$$C_D = \frac{\beta_1 \left( e^{-\beta_2 t} - e^{-\beta_3 t} \right)}{\beta_3 - \beta_2} \quad \ldots (C8)$$

where $\beta_i$ can be determined from experimental results using non-linear regression. Due to the fact that initial diglyceride concentration ($C_{D0}$) of fryer grease is not zero, the term $C_{D0}$ must be taken into account.

$$C_D = C_{D0} + \frac{\beta_1 \left( e^{-\beta_2 t} - e^{-\beta_3 t} \right)}{\beta_3 - \beta_2} \quad \ldots (C9)$$

After $t=t_{D1}$, diglyceride concentration went below its initial value, equation (C9) can not be used to predict $C_D$ at this period. We need to incorporate another term in this equation. Then

$$C_D = C_{D0} + \frac{\beta_1 \left( e^{-\beta_2 t} - e^{-\beta_3 t} \right)}{\beta_3 - \beta_2} - \frac{\beta_4 \left( e^{-\beta_5 t} - e^{-\beta_6 t} \right)}{\beta_6 - \beta_5} \quad \ldots (C10)$$

The ester concentration was derived in the same manner as we did for the diglyceride concentration except that the ester concentration never went below its initial concentration.

$$C_E = C_{E0} + \frac{\omega_1 \left( e^{-\omega_2 t} - e^{-\omega_3 t} \right)}{\omega_3 - \omega_2} \quad \ldots (C11)$$

Upon substitution of (C10) and (C11) into (C7):

$$\frac{dC_T}{dt} + k_1' C_T = k_2 \left[ \begin{array}{l} C_{D0} C_{E0} + C_{D0} \left( \frac{\omega_1}{\omega_3 - \omega_2} \right) \left( e^{-\omega_2 t} - e^{-\omega_3 t} \right) \\ + C_{E0} \left( \frac{\beta_1}{\beta_3 - \beta_2} \right) \left( e^{-\beta_2 t} - e^{-\beta_3 t} \right) \\ + \left( \frac{\beta_1}{\beta_3 - \beta_2} \right) \left( \frac{\omega_1}{\omega_3 - \omega_2} \right) \left( e^{-\beta_2 t} - e^{-\beta_3 t} \right) \left( e^{-\omega_2 t} - e^{-\omega_3 t} \right) \\ - C_{E0} \left( \frac{\beta_4}{\beta_6 - \beta_5} \right) \left( e^{-\beta_5 t} - e^{-\beta_6 t} \right) \\ - \left( \frac{\beta_4}{\beta_6 - \beta_5} \right) \left( \frac{\omega_1}{\omega_3 - \omega_2} \right) \left( e^{-\beta_5 t} - e^{-\beta_6 t} \right) \left( e^{-\omega_2 t} - e^{-\omega_3 t} \right) \end{array} \right] \quad \ldots \text{(C12)}$$

Rearranging:

$$\frac{dC_T}{dt} + k_1' C_T = k_2 \left[ \begin{array}{l} C_{D0} C_{E0} + C_{D0} \left( \frac{\omega_1}{\omega_3 - \omega_2} \right) \left( e^{-\omega_2 t} - e^{-\omega_3 t} \right) \\ + C_{E0} \left( \frac{\beta_1}{\beta_3 - \beta_2} \right) \left( e^{-\beta_2 t} - e^{-\beta_3 t} \right) \\ + \left( \frac{\beta_1}{\beta_3 - \beta_2} \right) \left( \frac{\omega_1}{\omega_3 - \omega_2} \right) \left( e^{-(\beta_2 + \omega_2) t} + e^{-(\beta_3 + \omega_3) t} - e^{-(\beta_2 + \omega_3) t} - e^{-(\beta_3 + \omega_2) t} \right) \\ - C_{E0} \left( \frac{\beta_4}{\beta_6 - \beta_5} \right) \left( e^{-\beta_5 t} - e^{-\beta_6 t} \right) \\ - \left( \frac{\beta_4}{\beta_6 - \beta_5} \right) \left( \frac{\omega_1}{\omega_3 - \omega_2} \right) \left( e^{-(\beta_5 + \omega_2) t} + e^{-(\beta_6 + \omega_3) t} - e^{-(\beta_5 + \omega_3) t} - e^{-(\beta_6 + \omega_2) t} \right) \end{array} \right]$$

… (C13)

Next, we let

$$C_1 = k_2 C_{D0} C_{E0}$$
$$C_2 = k_2 C_{E0}\left(\frac{\beta_1}{\beta_3 - \beta_2}\right)$$
$$C_3 = -k_2 C_{E0}\left(\frac{\beta_4}{\beta_6 - \beta_5}\right)$$
$$C_4 = k_2 C_{D0}\left(\frac{\omega_1}{\omega_3 - \omega_2}\right)$$
$$C_5 = k_2\left(\frac{\beta_1}{\beta_3 - \beta_2}\right)\left(\frac{\omega_1}{\omega_3 - \omega_2}\right)$$
$$C_6 = -k_2\left(\frac{\beta_4}{\beta_6 - \beta_5}\right)\left(\frac{\omega_1}{\omega_3 - \omega_2}\right)$$

$$\psi_1 = \beta_2 + \omega_2$$
$$\psi_2 = \beta_3 + \omega_3$$
$$\psi_3 = \beta_2 + \omega_3$$
$$\psi_4 = \beta_3 + \omega_2$$
$$\psi_5 = \beta_5 + \omega_2$$
$$\psi_6 = \beta_6 + \omega_3$$
$$\psi_7 = \beta_5 + \omega_3$$
$$\psi_8 = \beta_6 + \omega_2$$

so that equation (A13) can be written as

$$\frac{dC_T}{dt} + k_1' C_T = C_1 + C_2\left(e^{-\beta_2 t} - e^{-\beta_3 t}\right) + C_3\left(e^{-\beta_5 t} - e^{-\beta_6 t}\right) + C_4\left(e^{-\omega_2 t} - e^{-\omega_3 t}\right)$$
$$+ C_5\left(e^{-\psi_1 t} + e^{-\psi_2 t} - e^{-\psi_3 t} - e^{-\psi_4 t}\right) + C_6\left(e^{-\psi_5 t} + e^{-\psi_6 t} - e^{-\psi_7 t} - e^{-\psi_8 t}\right) \quad \ldots \text{(C14)}$$

Taking Laplace:

$$LC_T' + k_1' LC_T = C_1 L(1) + C_2\left(Le^{-\beta_2 t} - Le^{-\beta_3 t}\right) + C_3\left(Le^{-\beta_5 t} - Le^{-\beta_6 t}\right) + C_4\left(Le^{-\omega_2 t} - Le^{-\omega_3 t}\right)$$
$$+ C_5\left(Le^{-\psi_1 t} + Le^{-\psi_2 t} - Le^{-\psi_3 t} - Le^{-\psi_4 t}\right) + C_6\left(Le^{-\psi_5 t} + Le^{-\psi_6 t} - Le^{-\psi_7 t} - Le^{-\psi_8 t}\right) \quad \ldots \text{(C15)}$$

$$sLC_T - C_{T0} + k_1' LC_T = \frac{C_1}{s} + C_2\left(\frac{1}{s+\beta_2} - \frac{1}{s+\beta_3}\right) + C_3\left(\frac{1}{s+\beta_5} - \frac{1}{s+\beta_6}\right) + C_4\left(\frac{1}{s+\omega_2} - \frac{1}{s+\omega_3}\right)$$
$$+ C_5\left(\frac{1}{s+\psi_1} + \frac{1}{s+\psi_2} - \frac{1}{s+\psi_3} - \frac{1}{s+\psi_4}\right) + C_6\left(\frac{1}{s+\psi_5} + \frac{1}{s+\psi_6} - \frac{1}{s+\psi_7} - \frac{1}{s+\psi_8}\right)$$

$$
\begin{aligned}
LC_T = \frac{}{}
&C_1(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\psi_1)\\
&(s+\psi_2)(s+\psi_3)(s+\psi_4)(s+\psi_5)(s+\psi_6)(s+\psi_7)(s+\psi_8)\\
&+C_2 s(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\psi_1)\\
&(s+\psi_2)(s+\psi_3)(s+\psi_4)(s+\psi_5)(s+\psi_6)(s+\psi_7)(s+\psi_8)\\
&-C_2 s(s+\beta_2)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\psi_1)\\
&(s+\psi_2)(s+\psi_3)(s+\psi_4)(s+\psi_5)(s+\psi_6)(s+\psi_7)(s+\psi_8)\\
&+C_3 s(s+\beta_2)(s+\beta_3)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\psi_1)\\
&(s+\psi_2)(s+\psi_3)(s+\psi_4)(s+\psi_5)(s+\psi_6)(s+\psi_7)(s+\psi_8)\\
&-C_3 s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\omega_2)(s+\omega_3)(s+\psi_1)\\
&(s+\psi_2)(s+\psi_3)(s+\psi_4)(s+\psi_5)(s+\psi_6)(s+\psi_7)(s+\psi_8)\\
&+C_4 s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_3)(s+\psi_1)\\
&(s+\psi_2)(s+\psi_3)(s+\psi_4)(s+\psi_5)(s+\psi_6)(s+\psi_7)(s+\psi_8)\\
&-C_4 s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\psi_1)\\
&(s+\psi_2)(s+\psi_3)(s+\psi_4)(s+\psi_5)(s+\psi_6)(s+\psi_7)(s+\psi_8)\\
&+C_5 s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)\\
&(s+\psi_2)(s+\psi_3)(s+\psi_4)(s+\psi_5)(s+\psi_6)(s+\psi_7)(s+\psi_8)\\
&+C_5 s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\psi_1)\\
&(s+\psi_3)(s+\psi_4)(s+\psi_5)(s+\psi_6)(s+\psi_7)(s+\psi_8)\\
&-C_5 s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\psi_1)\\
&(s+\psi_2)(s+\psi_4)(s+\psi_5)(s+\psi_6)(s+\psi_7)(s+\psi_8)\\
&-C_5 s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\psi_1)\\
&(s+\psi_2)(s+\psi_3)(s+\psi_5)(s+\psi_6)(s+\psi_7)(s+\psi_8)\\
&+C_6 s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\psi_1)\\
&(s+\psi_2)(s+\psi_3)(s+\psi_4)(s+\psi_6)(s+\psi_7)(s+\psi_8)\\
&+C_6 s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\psi_1)\\
&(s+\psi_2)(s+\psi_3)(s+\psi_4)(s+\psi_5)(s+\psi_7)(s+\psi_8)\\
&-C_6 s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\psi_1)\\
&(s+\psi_2)(s+\psi_3)(s+\psi_4)(s+\psi_5)(s+\psi_6)(s+\psi_8)\\
&-C_6 s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\psi_1)\\
&(s+\psi_2)(s+\psi_3)(s+\psi_4)(s+\psi_5)(s+\psi_6)(s+\psi_7)\\
&+C_{T0} s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\psi_1)\\
&(s+\psi_2)(s+\psi_3)(s+\psi_4)(s+\psi_5)(s+\psi_6)(s+\psi_7)(s+\psi_8)\\
\hline
&s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\psi_1)\\
&(s+\psi_2)(s+\psi_3)(s+\psi_4)(s+\psi_5)(s+\psi_6)(s+\psi_7)(s+\psi_8)(s+k_1')
\end{aligned}
$$

… (C16)

Using the partial fraction technique:

$$LC_T = \frac{A_1}{s} + \frac{A_2}{(s+\beta_2)} + \frac{A_3}{(s+\beta_3)} + \frac{A_4}{(s+\beta_5)} + \frac{A_5}{(s+\beta_6)} + \frac{A_6}{(s+\omega_2)} + \frac{A_7}{(s+\omega_3)} + \frac{A_8}{(s+\psi_1)}$$
$$+ \frac{A_9}{(s+\psi_2)} + \frac{A_{10}}{(s+\psi_3)} + \frac{A_{11}}{(s+\psi_4)} + \frac{A_{12}}{(s+\psi_5)} + \frac{A_{13}}{(s+\psi_6)} + \frac{A_{14}}{(s+\psi_7)} + \frac{A_{15}}{(s+\psi_8)} + \frac{A_{16}}{(s+k_1')}$$

… (C17)

Taking inverse Laplace:

$$C_T = A_1 + A_2 e^{-\beta_2 t} + A_3 e^{-\beta_3 t} + A_4 e^{-\beta_5 t} + A_5 e^{-\beta_6 t} + A_6 e^{-\omega_2 t} + A_7 e^{-\omega_3 t}$$
$$+ A_8 e^{-\psi_1 t} + A_9 e^{-\psi_2 t} + A_{10} e^{-\psi_3 t} + A_{11} e^{-\psi_4 t} + A_{12} e^{-\psi_5 t} + A_{13} e^{-\psi_6 t} + A_{14} e^{-\psi_7 t} \quad \text{… (C18)}$$
$$+ A_{15} e^{-\psi_8 t} + A_{16} e^{-k_1' t}$$

From equation (C16) and C(17), *let* $s = 0$

$$A_1 = \frac{C_1}{k_1'}$$

*Let* $s = -\beta_2$

$$A_2 = \frac{C_2}{k_1' - \beta_2}$$

*Let* $s = -\beta_3$

$$A_3 = -\frac{C_2}{k_1' - \beta_3}$$

*Let* $s = -\beta_5$

$$A_4 = \frac{C_3}{k_1' - \beta_5}$$

$$Let \quad s = -\beta_6$$

$$A_5 = -\frac{C_3}{k_1 - \beta_6}$$

$$Let \quad s = -\omega_2$$

$$A_6 = \frac{C_4}{k_1' - \omega_2}$$

$$Let \quad s = -\omega_3$$

$$A_7 = -\frac{C_4}{k_1' - \omega_3}$$

$$Let \quad s = -\psi_1$$

$$A_8 = \frac{C_5}{k_1' - \psi_1}$$

$$Let \quad s = -\psi_2$$

$$A_9 = \frac{C_5}{k_1' - \psi_2}$$

$$Let \quad s = -\psi_3$$

$$A_{10} = -\frac{C_5}{k_1' - \psi_3}$$

$$Let \quad s = -\psi_4$$

$$A_{11} = -\frac{C_5}{k_1' - \psi_4}$$

$$Let \quad s = -\psi_5$$

$$A_{12} = \frac{C_6}{k_1' - \psi_5}$$

*Let* $s = -\psi_6$

$$A_{13} = \frac{C_6}{k_1' - \psi_6}$$

*Let* $s = -\psi_7$

$$A_{14} = -\frac{C_6}{k_1' - \psi_7}$$

*Let* $s = -\psi_8$

$$A_{15} = -\frac{C_6}{k_1' - \psi_8}$$

*Let* $s = -k_1'$

$$A_{16} = -\frac{C_1}{k_1'} - \frac{C_2}{k_1' - \beta_2} + \frac{C_2}{k_1' - \beta_3} - \frac{C_3}{k_1' - \beta_5} + \frac{C_3}{k_1' - \beta_6} - \frac{C_4}{k_1' - \omega_2} + \frac{C_4}{k_1' - \omega_3}$$
$$- \frac{C_5}{k_1' - \psi_1} - \frac{C_5}{k_1' - \psi_2} + \frac{C_5}{k_1' - \psi_3} + \frac{C_5}{k_1' - \psi_4} - \frac{C_6}{k_1' - \psi_5} - \frac{C_6}{k_1' - \psi_6} + \frac{C_6}{k_1' - \psi_7}$$
$$+ \frac{C_6}{k_1' - \psi_8} + C_{T0}$$

$$A_{16} = -A_1 - A_2 - A_3 - A_4 - A_5 - A_6 - A_7 - A_8 - A_9$$
$$- A_{10} - A_{11} - A_{12} - A_{13} - A_{14} - A_{15} + C_{T0}$$

Substitute $A_i$, $C_i$, and $\psi_i$ into equation (C18):

$$C_T = \frac{k_2 C_{D0} C_{E0}}{k_1'} + \frac{k_2 C_{E0}\left(\frac{\beta_1}{\beta_3 - \beta_2}\right)}{k_1' - \beta_2} e^{-\beta_2 t} - \frac{k_2 C_{E0}\left(\frac{\beta_1}{\beta_3 - \beta_2}\right)}{k_1' - \beta_3} e^{-\beta_3 t}$$
$$- \frac{k_2 C_{E0}\left(\frac{\beta_4}{\beta_6 - \beta_5}\right)}{k_1' - \beta_5} e^{-\beta_5 t} + \frac{k_2 C_{E0}\left(\frac{\beta_4}{\beta_6 - \beta_5}\right)}{k_1' - \beta_6} e^{-\beta_6 t} + \frac{k_2 C_{D0}\left(\frac{\omega_1}{\omega_3 - \omega_2}\right)}{k_1' - \omega_2} e^{-\omega_2 t}$$
$$- \frac{k_2 C_{D0}\left(\frac{\omega_1}{\omega_3 - \omega_2}\right)}{k_1' - \omega_3} e^{-\omega_3 t} + \frac{k_2\left(\frac{\beta_1}{\beta_3 - \beta_2}\right)\left(\frac{\omega_1}{\omega_3 - \omega_2}\right)}{k_1' - (\beta_2 + \omega_2)} e^{-(\beta_2 + \omega_2)t}$$

$$+ \frac{k_2\left(\frac{\beta_1}{\beta_3 - \beta_2}\right)\left(\frac{\omega_1}{\omega_3 - \omega_2}\right)}{k_1' - (\beta_3 + \omega_3)} e^{-(\beta_3 + \omega_3)t} - \frac{k_2\left(\frac{\beta_1}{\beta_3 - \beta_2}\right)\left(\frac{\omega_1}{\omega_3 - \omega_2}\right)}{k_1' - (\beta_2 + \omega_3)} e^{-(\beta_2 + \omega_3)t}$$
$$- \frac{k_2\left(\frac{\beta_1}{\beta_3 - \beta_2}\right)\left(\frac{\omega_1}{\omega_3 - \omega_2}\right)}{k_1' - (\beta_3 + \omega_2)} e^{-(\beta_3 + \omega_2)t} - \frac{k_2\left(\frac{\beta_4}{\beta_6 - \beta_5}\right)\left(\frac{\omega_1}{\omega_3 - \omega_2}\right)}{k_1' - (\beta_5 + \omega_2)} e^{-(\beta_5 + \omega_2)t}$$
$$- \frac{k_2\left(\frac{\beta_4}{\beta_6 - \beta_5}\right)\left(\frac{\omega_1}{\omega_3 - \omega_2}\right)}{k_1' - (\beta_6 + \omega_3)} e^{-(\beta_6 + \omega_3)t} + \frac{k_2\left(\frac{\beta_4}{\beta_6 - \beta_5}\right)\left(\frac{\omega_1}{\omega_3 - \omega_2}\right)}{k_1' - (\beta_5 + \omega_3)} e^{-(\beta_5 + \omega_3)t}$$
$$+ \frac{k_2\left(\frac{\beta_4}{\beta_6 - \beta_5}\right)\left(\frac{\omega_1}{\omega_3 - \omega_2}\right)}{k_1' - (\beta_6 + \omega_2)} e^{-(\beta_6 + \omega_2)t}$$

$$
+\left[\begin{array}{l}
-\dfrac{(k_2 C_{D0} C_{E0})}{k_1'}-\dfrac{\left(k_2 C_{E0}\left(\dfrac{\beta_1}{\beta_3-\beta_2}\right)\right)}{k_1'-\beta_2}+\dfrac{\left(k_2 C_{E0}\left(\dfrac{\beta_1}{\beta_3-\beta_2}\right)\right)}{k_1'-\beta_3} \\
-\dfrac{\left(-k_2 C_{E0}\left(\dfrac{\beta_4}{\beta_6-\beta_5}\right)\right)}{k_1'-\beta_5}+\dfrac{\left(-k_2 C_{E0}\left(\dfrac{\beta_4}{\beta_6-\beta_5}\right)\right)}{k_1'-\beta_6} \\
-\dfrac{\left(k_2 C_{D0}\left(\dfrac{\omega_1}{\omega_3-\omega_2}\right)\right)}{k_1'-\omega_2}+\dfrac{\left(k_2 C_{D0}\left(\dfrac{\omega_1}{\omega_3-\omega_2}\right)\right)}{k_1'-\omega_3} \\
-\dfrac{\left(k_2\left(\dfrac{\beta_1}{\beta_3-\beta_2}\right)\left(\dfrac{\omega_1}{\omega_3-\omega_2}\right)\right)}{k_1'-(\beta_2+\omega_2)}-\dfrac{\left(k_2\left(\dfrac{\beta_1}{\beta_3-\beta_2}\right)\left(\dfrac{\omega_1}{\omega_3-\omega_2}\right)\right)}{k_1'-(\beta_3+\omega_3)} \\
+\dfrac{\left(k_2\left(\dfrac{\beta_1}{\beta_3-\beta_2}\right)\left(\dfrac{\omega_1}{\omega_3-\omega_2}\right)\right)}{k_1'-(\beta_2+\omega_3)}+\dfrac{\left(k_2\left(\dfrac{\beta_1}{\beta_3-\beta_2}\right)\left(\dfrac{\omega_1}{\omega_3-\omega_2}\right)\right)}{k_1'-(\beta_3+\omega_2)} \\
-\dfrac{\left(-k_2\left(\dfrac{\beta_4}{\beta_6-\beta_5}\right)\left(\dfrac{\omega_1}{\omega_3-\omega_2}\right)\right)}{k_1'-(\beta_5+\omega_2)}-\dfrac{\left(-k_2\left(\dfrac{\beta_4}{\beta_6-\beta_5}\right)\left(\dfrac{\omega_1}{\omega_3-\omega_2}\right)\right)}{k_1'-(\beta_6+\omega_3)} \\
+\dfrac{\left(-k_2\left(\dfrac{\beta_4}{\beta_6-\beta_5}\right)\left(\dfrac{\omega_1}{\omega_3-\omega_2}\right)\right)}{k_1'-(\beta_5+\omega_3)}+\dfrac{\left(-k_2\left(\dfrac{\beta_4}{\beta_6-\beta_5}\right)\left(\dfrac{\omega_1}{\omega_3-\omega_2}\right)\right)}{k_1'-(\beta_6+\omega_2)}+C_{T0}
\end{array}\right] e^{-k_1 t}
$$

… (C19)

Equation (C19) is the solution to equation (C7). The two unknown parameters $k_1$ and $k_2$ can be calculated by means of a non-linear regression.

Determination of $k_3$ and $k_4$

The rate of concentration change of diglyceride is rate of formation of diglyceride in (C1) and (C4) subtract rate of disappearance of diglyceride in (C2) and (C3):

$$\frac{dC_D}{dt} = k_1' C_T - k_2 C_D C_E - k_3' C_D + k_4 C_M C_E \quad \ldots \quad \text{(C20)}$$

Similar to equation (C10), the concentration of triglyceride and monoglyceride can be expressed as:

$$C_T = C_{T0} + \frac{\eta_1 \left( e^{-\eta_2 t} - e^{-\eta_3 t} \right)}{\eta_3 - \eta_2} \quad \ldots \text{(C21)}$$

$$C_M = C_{M0} + \frac{\alpha_1 \left( e^{-\alpha_2 t} - e^{-\alpha_3 t} \right)}{\alpha_3 - \alpha_2} - \frac{\alpha_4 \left( e^{-\alpha_5 t} - e^{-\alpha_6 t} \right)}{\alpha_6 - \alpha_5} \quad \ldots \text{(C22)}$$

From equation (C7) and (C14):

$$\begin{aligned} k_2 C_D C_E = {} & C_1 + C_2 \left( e^{-\beta_2 t} - e^{-\beta_3 t} \right) + C_3 \left( e^{-\beta_5 t} - e^{-\beta_6 t} \right) + C_4 \left( e^{-\omega_2 t} - e^{-\omega_3 t} \right) \\ & + C_5 \left( e^{-\psi_1 t} + e^{-\psi_2 t} - e^{-\psi_3 t} - e^{-\psi_4 t} \right) + C_6 \left( e^{-\psi_5 t} + e^{-\psi_6 t} - e^{-\psi_7 t} - e^{-\psi_8 t} \right) \end{aligned} \quad \ldots \text{(C23)}$$

Substitute (C11), (C21), C(22), and C(23) into (C20):

$$\begin{aligned} & \frac{dC_D}{dt} + k_3' C_D = k_1' \left( C_{T0} + \frac{\eta_1 \left( e^{-\eta_2 t} - e^{-\eta_3 t} \right)}{\eta_3 - \eta_2} \right) \\ & - C_1 - C_2 \left( e^{-\beta_2 t} - e^{-\beta_3 t} \right) - C_3 \left( e^{-\beta_5 t} - e^{-\beta_6 t} \right) - C_4 \left( e^{-\omega_2 t} - e^{-\omega_3 t} \right) \\ & - C_5 \left( e^{-\psi_1 t} + e^{-\psi_2 t} - e^{-\psi_3 t} - e^{-\psi_4 t} \right) - C_6 \left( e^{-\psi_5 t} + e^{-\psi_6 t} - e^{-\psi_7 t} - e^{-\psi_8 t} \right) \\ & + k_4 \left( C_{M0} + \frac{\alpha_1 \left( e^{-\alpha_2 t} - e^{-\alpha_3 t} \right)}{\alpha_3 - \alpha_2} - \frac{\alpha_4 \left( e^{-\alpha_5 t} - e^{-\alpha_6 t} \right)}{\alpha_6 - \alpha_5} \right) \left( C_{E0} + \frac{\omega_1 \left( e^{-\omega_2 t} - e^{-\omega_3 t} \right)}{\omega_3 - \omega_2} \right) \end{aligned}$$

$$\frac{dC_D}{dt} + k_3' C_D = -C_1 - C_2\left(e^{-\beta_2 t} - e^{-\beta_3 t}\right) - C_3\left(e^{-\beta_5 t} - e^{-\beta_6 t}\right) - C_4\left(e^{-\omega_2 t} - e^{-\omega_3 t}\right)$$
$$- C_5\left(e^{-\psi_1 t} + e^{-\psi_2 t} - e^{-\psi_3 t} - e^{-\psi_4 t}\right) - C_6\left(e^{-\psi_5 t} + e^{-\psi_6 t} - e^{-\psi_7 t} - e^{-\psi_8 t}\right)$$
$$+ k_1' C_{T0} + k_1'\left(\frac{\eta_1}{\eta_3 - \eta_2}\right)\left(e^{-\eta_2 t} - e^{-\eta_3 t}\right) + k_4 C_{M0} C_{E0} + k_4 C_{M0}\left(\frac{\omega_1}{\omega_3 - \omega_2}\right)\left(e^{-\omega_2 t} - e^{-\omega_3 t}\right)$$
$$+ k_4 C_{E0}\left(\frac{\alpha_1}{\alpha_3 - \alpha_2}\right)\left(e^{-\alpha_2 t} - e^{-\alpha_3 t}\right) + k_4\left(\frac{\alpha_1}{\alpha_3 - \alpha_2}\right)\left(\frac{\omega_1}{\omega_3 - \omega_2}\right)\left(e^{-\alpha_2 t} - e^{-\alpha_3 t}\right)\left(e^{-\omega_2 t} - e^{-\omega_3 t}\right)$$
$$- k_4 C_{E0}\left(\frac{\alpha_4}{\alpha_6 - \alpha_5}\right)\left(e^{-\alpha_5 t} - e^{-\alpha_6 t}\right) - k_4\left(\frac{\alpha_4}{\alpha_6 - \alpha_5}\right)\left(\frac{\omega_1}{\omega_3 - \omega_2}\right)\left(e^{-\alpha_5 t} - e^{-\alpha_6 t}\right)\left(e^{-\omega_2 t} - e^{-\omega_3 t}\right)$$

Next, we let

$$C_7 = k_1'\left(\frac{\eta_1}{\eta_3 - \eta_2}\right)$$
$$C_8 = k_4 C_{M0}\left(\frac{\omega_1}{\omega_3 - \omega_2}\right)$$
$$C_9 = k_4 C_{E0}\left(\frac{\alpha_1}{\alpha_3 - \alpha_2}\right)$$
$$C_{10} = -k_4 C_{E0}\left(\frac{\alpha_4}{\alpha_6 - \alpha_5}\right)$$
$$C_{11} = k_4\left(\frac{\alpha_1}{\alpha_3 - \alpha_2}\right)\left(\frac{\omega_1}{\omega_3 - \omega_2}\right)$$
$$C_{12} = -k_4\left(\frac{\alpha_4}{\alpha_6 - \alpha_5}\right)\left(\frac{\omega_1}{\omega_3 - \omega_2}\right)$$
$$C_{13} = k_1' C_{T0} + k_4 C_{M0} C_{E0}$$

$$\psi_9 = \alpha_2 + \omega_2$$
$$\psi_{10} = \alpha_3 + \omega_3$$
$$\psi_{11} = \alpha_2 + \omega_3$$
$$\psi_{12} = \alpha_3 + \omega_2$$
$$\psi_{13} = \alpha_5 + \omega_2$$
$$\psi_{14} = \alpha_6 + \omega_3$$
$$\psi_{15} = \alpha_5 + \omega_3$$
$$\psi_{16} = \alpha_6 + \omega_2$$

Then,

$$\frac{dC_D}{dt} + k_3' C_D = -C_1 - C_2\left(e^{-\beta_2 t} - e^{-\beta_3 t}\right) - C_3\left(e^{-\beta_5 t} - e^{-\beta_6 t}\right) - C_4\left(e^{-\omega_2 t} - e^{-\omega_3 t}\right)$$
$$- C_5\left(e^{-\psi_1 t} + e^{-\psi_2 t} - e^{-\psi_3 t} - e^{-\psi_4 t}\right) - C_6\left(e^{-\psi_5 t} + e^{-\psi_6 t} - e^{-\psi_7 t} - e^{-\psi_8 t}\right)$$
$$+ C_7\left(e^{-\eta_2 t} - e^{-\eta_3 t}\right) + C_8\left(e^{-\omega_2 t} - e^{-\omega_3 t}\right) + C_9\left(e^{-\alpha_2 t} - e^{-\alpha_3 t}\right)$$
$$+ C_{10}\left(e^{-\alpha_5 t} - e^{-\alpha_6 t}\right) + C_{11}\left(e^{-\alpha_2 t} - e^{-\alpha_3 t}\right)\left(e^{-\omega_2 t} - e^{-\omega_3 t}\right)$$
$$+ C_{12}\left(e^{-\alpha_5 t} - e^{-\alpha_6 t}\right)\left(e^{-\omega_2 t} - e^{-\omega_3 t}\right) + C_{13}$$

$$\frac{dC_D}{dt} + k_3' C_D = C_{13} - C_1 - C_2\left(e^{-\beta_2 t} - e^{-\beta_3 t}\right) - C_3\left(e^{-\beta_5 t} - e^{-\beta_6 t}\right) + \left(C_8 - C_4\right)\left(e^{-\omega_2 t} - e^{-\omega_3 t}\right)$$
$$+ C_9\left(e^{-\alpha_2 t} - e^{-\alpha_3 t}\right) + C_{10}\left(e^{-\alpha_5 t} - e^{-\alpha_6 t}\right) + C_7\left(e^{-\eta_2 t} - e^{-\eta_3 t}\right)$$
$$- C_5\left(e^{-\psi_1 t} + e^{-\psi_2 t} - e^{-\psi_3 t} - e^{-\psi_4 t}\right) - C_6\left(e^{-\psi_5 t} + e^{-\psi_6 t} - e^{-\psi_7 t} - e^{-\psi_8 t}\right)$$
$$+ C_{11}\left(e^{-\psi_9 t} + e^{-\psi_{10} t} - e^{-\psi_{11} t} - e^{-\psi_{12} t}\right) + C_{12}\left(e^{-\psi_{13} t} + e^{-\psi_{14} t} - e^{-\psi_{15} t} - e^{-\psi_{16} t}\right)$$

… (C24).

Taking Laplace:

$$LC_D^{'} + k_3' LC_D = (C_{13} - C_1)L(1) - C_2\left(Le^{-\beta_2 t} - Le^{-\beta_3 t}\right) - C_3\left(Le^{-\beta_5 t} - Le^{-\beta_6 t}\right)$$
$$+ (C_8 - C_4)\left(Le^{-\omega_2 t} - Le^{-\omega_3 t}\right) + C_9\left(Le^{-\alpha_2 t} - Le^{-\alpha_3 t}\right) + C_{10}\left(Le^{-\alpha_5 t} - Le^{-\alpha_6 t}\right)$$
$$+ C_7\left(Le^{-\eta_2 t} - Le^{-\eta_3 t}\right) - C_5\left(Le^{-\psi_1 t} + Le^{-\psi_2 t} - Le^{-\psi_3 t} - Le^{-\psi_4 t}\right)$$
$$- C_6\left(Le^{-\psi_5 t} + Le^{-\psi_6 t} - Le^{-\psi_7 t} - Le^{-\psi_8 t}\right) + C_{11}\left(Le^{-\psi_9 t} + Le^{-\psi_{10} t} - Le^{-\psi_{11} t} - Le^{-\psi_{12} t}\right)$$
$$+ C_{12}\left(Le^{-\psi_{13} t} + Le^{-\psi_{14} t} - Le^{-\psi_{15} t} - Le^{-\psi_{16} t}\right)$$

$$sLC_D - C_{D0} + k_3' LC_D = \frac{(C_{13} - C_1)}{s} - \frac{C_2}{s+\beta_2} + \frac{C_2}{s+\beta_3} - \frac{C_3}{s+\beta_5} + \frac{C_3}{s+\beta_6}$$
$$+ \frac{(C_8 - C_4)}{s+\omega_2} - \frac{(C_8 - C_4)}{s+\omega_3} + \frac{C_9}{s+\alpha_2} - \frac{C_9}{s+\alpha_3} + \frac{C_{10}}{s+\alpha_5} - \frac{C_{10}}{s+\alpha_6}$$
$$+ \frac{C_7}{s+\eta_2} - \frac{C_7}{s+\eta_3} - \frac{C_5}{s+\psi_1} - \frac{C_5}{s+\psi_2} + \frac{C_5}{s+\psi_3} + \frac{C_5}{s+\psi_4}$$
$$- \frac{C_6}{s+\psi_5} - \frac{C_6}{s+\psi_6} + \frac{C_6}{s+\psi_7} + \frac{C_6}{s+\psi_8} + \frac{C_{11}}{s+\psi_9} + \frac{C_{11}}{s+\psi_{10}} - \frac{C_{11}}{s+\psi_{11}} - \frac{C_{11}}{s+\psi_{12}}$$
$$+ \frac{C_{12}}{s+\psi_{13}} + \frac{C_{12}}{s+\psi_{14}} - \frac{C_{12}}{s+\psi_{15}} - \frac{C_{12}}{s+\psi_{16}}$$

$$
\begin{aligned}
&LC_D = \\
&(C_{13} - C_1)(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\alpha_2)(s+\alpha_3)(s+\alpha_5)(s+\alpha_6) \\
&(s+\eta_2)(s+\eta_3)(s+\psi_1)(s+\psi_2)(s+\psi_3)(s+\psi_4)(s+\psi_5)(s+\psi_6)(s+\psi_7)(s+\psi_8) \\
&(s+\psi_9)(s+\psi_{10})(s+\psi_{11})(s+\psi_{12})(s+\psi_{13})(s+\psi_{14})(s+\psi_{15})(s+\psi_{16}) \\
&- C_2 s(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\alpha_2)(s+\alpha_3)(s+\alpha_5)(s+\alpha_6) \\
&(s+\eta_2)(s+\eta_3)(s+\psi_1)(s+\psi_2)(s+\psi_3)(s+\psi_4)(s+\psi_5)(s+\psi_6)(s+\psi_7)(s+\psi_8) \\
&(s+\psi_9)(s+\psi_{10})(s+\psi_{11})(s+\psi_{12})(s+\psi_{13})(s+\psi_{14})(s+\psi_{15})(s+\psi_{16}) \\
&+ C_2 s(s+\beta_2)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\alpha_2)(s+\alpha_3)(s+\alpha_5)(s+\alpha_6) \\
&(s+\eta_2)(s+\eta_3)(s+\psi_1)(s+\psi_2)(s+\psi_3)(s+\psi_4)(s+\psi_5)(s+\psi_6)(s+\psi_7)(s+\psi_8) \\
&(s+\psi_9)(s+\psi_{10})(s+\psi_{11})(s+\psi_{12})(s+\psi_{13})(s+\psi_{14})(s+\psi_{15})(s+\psi_{16}) \\
&- C_3 s(s+\beta_2)(s+\beta_3)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\alpha_2)(s+\alpha_3)(s+\alpha_5)(s+\alpha_6) \\
&(s+\eta_2)(s+\eta_3)(s+\psi_1)(s+\psi_2)(s+\psi_3)(s+\psi_4)(s+\psi_5)(s+\psi_6)(s+\psi_7)(s+\psi_8) \\
&(s+\psi_9)(s+\psi_{10})(s+\psi_{11})(s+\psi_{12})(s+\psi_{13})(s+\psi_{14})(s+\psi_{15})(s+\psi_{16}) \\
&+ C_3 s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\omega_2)(s+\omega_3)(s+\alpha_2)(s+\alpha_3)(s+\alpha_5)(s+\alpha_6) \\
&(s+\eta_2)(s+\eta_3)(s+\psi_1)(s+\psi_2)(s+\psi_3)(s+\psi_4)(s+\psi_5)(s+\psi_6)(s+\psi_7)(s+\psi_8) \\
&(s+\psi_9)(s+\psi_{10})(s+\psi_{11})(s+\psi_{12})(s+\psi_{13})(s+\psi_{14})(s+\psi_{15})(s+\psi_{16}) \\
&+ (C_8 - C_4)s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_3)(s+\alpha_2)(s+\alpha_3)(s+\alpha_5)(s+\alpha_6) \\
&(s+\eta_2)(s+\eta_3)(s+\psi_1)(s+\psi_2)(s+\psi_3)(s+\psi_4)(s+\psi_5)(s+\psi_6)(s+\psi_7)(s+\psi_8) \\
&(s+\psi_9)(s+\psi_{10})(s+\psi_{11})(s+\psi_{12})(s+\psi_{13})(s+\psi_{14})(s+\psi_{15})(s+\psi_{16}) \\
&- (C_8 - C_4)s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\alpha_2)(s+\alpha_3)(s+\alpha_5)(s+\alpha_6) \\
&(s+\eta_2)(s+\eta_3)(s+\psi_1)(s+\psi_2)(s+\psi_3)(s+\psi_4)(s+\psi_5)(s+\psi_6)(s+\psi_7)(s+\psi_8) \\
&(s+\psi_9)(s+\psi_{10})(s+\psi_{11})(s+\psi_{12})(s+\psi_{13})(s+\psi_{14})(s+\psi_{15})(s+\psi_{16}) \\
&C_9 s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\alpha_3)(s+\alpha_5)(s+\alpha_6) \\
&(s+\eta_2)(s+\eta_3)(s+\psi_1)(s+\psi_2)(s+\psi_3)(s+\psi_4)(s+\psi_5)(s+\psi_6)(s+\psi_7)(s+\psi_8) \\
&(s+\psi_9)(s+\psi_{10})(s+\psi_{11})(s+\psi_{12})(s+\psi_{13})(s+\psi_{14})(s+\psi_{15})(s+\psi_{16}) \\
&- C_9 s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\alpha_2)(s+\alpha_5)(s+\alpha_6) \\
&(s+\eta_2)(s+\eta_3)(s+\psi_1)(s+\psi_2)(s+\psi_3)(s+\psi_4)(s+\psi_5)(s+\psi_6)(s+\psi_7)(s+\psi_8) \\
&(s+\psi_9)(s+\psi_{10})(s+\psi_{11})(s+\psi_{12})(s+\psi_{13})(s+\psi_{14})(s+\psi_{15})(s+\psi_{16}) \\
&+ C_{10} s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\alpha_2)(s+\alpha_3)(s+\alpha_6) \\
&(s+\eta_2)(s+\eta_3)(s+\psi_1)(s+\psi_2)(s+\psi_3)(s+\psi_4)(s+\psi_5)(s+\psi_6)(s+\psi_7)(s+\psi_8) \\
&(s+\psi_9)(s+\psi_{10})(s+\psi_{11})(s+\psi_{12})(s+\psi_{13})(s+\psi_{14})(s+\psi_{15})(s+\psi_{16}) \\
&- C_{10} s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\alpha_2)(s+\alpha_3)(s+\alpha_5) \\
&(s+\eta_2)(s+\eta_3)(s+\psi_1)(s+\psi_2)(s+\psi_3)(s+\psi_4)(s+\psi_5)(s+\psi_6)(s+\psi_7)(s+\psi_8) \\
&(s+\psi_9)(s+\psi_{10})(s+\psi_{11})(s+\psi_{12})(s+\psi_{13})(s+\psi_{14})(s+\psi_{15})(s+\psi_{16}) \\
&+ C_7 s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\alpha_2)(s+\alpha_3)(s+\alpha_5)(s+\alpha_6) \\
&(s+\eta_3)(s+\psi_1)(s+\psi_2)(s+\psi_3)(s+\psi_4)(s+\psi_5)(s+\psi_6)(s+\psi_7)(s+\psi_8) \\
&(s+\psi_9)(s+\psi_{10})(s+\psi_{11})(s+\psi_{12})(s+\psi_{13})(s+\psi_{14})(s+\psi_{15})(s+\psi_{16}) \\
&- C_7 s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\alpha_2)(s+\alpha_3)(s+\alpha_5)(s+\alpha_6) \\
&(s+\eta_2)(s+\psi_1)(s+\psi_2)(s+\psi_3)(s+\psi_4)(s+\psi_5)(s+\psi_6)(s+\psi_7)(s+\psi_8) \\
&(s+\psi_9)(s+\psi_{10})(s+\psi_{11})(s+\psi_{12})(s+\psi_{13})(s+\psi_{14})(s+\psi_{15})(s+\psi_{16}) \\
&- C_5 s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\alpha_2)(s+\alpha_3)(s+\alpha_5)(s+\alpha_6) \\
&(s+\eta_2)(s+\eta_3)(s+\psi_2)(s+\psi_3)(s+\psi_4)(s+\psi_5)(s+\psi_6)(s+\psi_7)(s+\psi_8) \\
&(s+\psi_9)(s+\psi_{10})(s+\psi_{11})(s+\psi_{12})(s+\psi_{13})(s+\psi_{14})(s+\psi_{15})(s+\psi_{16}) \\
&- C_5 s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\alpha_2)(s+\alpha_3)(s+\alpha_5)(s+\alpha_6) \\
&(s+\eta_2)(s+\eta_3)(s+\psi_1)(s+\psi_3)(s+\psi_4)(s+\psi_5)(s+\psi_6)(s+\psi_7)(s+\psi_8) \\
&(s+\psi_9)(s+\psi_{10})(s+\psi_{11})(s+\psi_{12})(s+\psi_{13})(s+\psi_{14})(s+\psi_{15})(s+\psi_{16}) \\
&+ C_5 s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\alpha_2)(s+\alpha_3)(s+\alpha_5)(s+\alpha_6) \\
&(s+\eta_2)(s+\eta_3)(s+\psi_1)(s+\psi_2)(s+\psi_4)(s+\psi_5)(s+\psi_6)(s+\psi_7)(s+\psi_8) \\
&(s+\psi_9)(s+\psi_{10})(s+\psi_{11})(s+\psi_{12})(s+\psi_{13})(s+\psi_{14})(s+\psi_{15})(s+\psi_{16}) \\
&+ C_5 s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\alpha_2)(s+\alpha_3)(s+\alpha_5)(s+\alpha_6) \\
&(s+\eta_2)(s+\eta_3)(s+\psi_1)(s+\psi_2)(s+\psi_3)(s+\psi_5)(s+\psi_6)(s+\psi_7)(s+\psi_8) \\
&(s+\psi_9)(s+\psi_{10})(s+\psi_{11})(s+\psi_{12})(s+\psi_{13})(s+\psi_{14})(s+\psi_{15})(s+\psi_{16})
\end{aligned}
$$

$$
\begin{aligned}
&-C_6 s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\alpha_2)(s+\alpha_3)(s+\alpha_5)(s+\alpha_6)\\
&(s+\eta_2)(s+\eta_3)(s+\psi_1)(s+\psi_2)(s+\psi_3)(s+\psi_4)(s+\psi_6)(s+\psi_7)(s+\psi_8)\\
&(s+\psi_9)(s+\psi_{10})(s+\psi_{11})(s+\psi_{12})(s+\psi_{13})(s+\psi_{14})(s+\psi_{15})(s+\psi_{16})\\
&-C_6 s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\alpha_2)(s+\alpha_3)(s+\alpha_5)(s+\alpha_6)\\
&(s+\eta_2)(s+\eta_3)(s+\psi_1)(s+\psi_2)(s+\psi_3)(s+\psi_4)(s+\psi_5)(s+\psi_7)(s+\psi_8)\\
&(s+\psi_9)(s+\psi_{10})(s+\psi_{11})(s+\psi_{12})(s+\psi_{13})(s+\psi_{14})(s+\psi_{15})(s+\psi_{16})\\
&+C_6 s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\alpha_2)(s+\alpha_3)(s+\alpha_5)(s+\alpha_6)\\
&(s+\eta_2)(s+\eta_3)(s+\psi_1)(s+\psi_2)(s+\psi_3)(s+\psi_4)(s+\psi_5)(s+\psi_6)(s+\psi_8)\\
&(s+\psi_9)(s+\psi_{10})(s+\psi_{11})(s+\psi_{12})(s+\psi_{13})(s+\psi_{14})(s+\psi_{15})(s+\psi_{16})\\
&+C_6 s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\alpha_2)(s+\alpha_3)(s+\alpha_5)(s+\alpha_6)\\
&(s+\eta_2)(s+\eta_3)(s+\psi_1)(s+\psi_2)(s+\psi_3)(s+\psi_4)(s+\psi_5)(s+\psi_6)(s+\psi_7)\\
&(s+\psi_9)(s+\psi_{10})(s+\psi_{11})(s+\psi_{12})(s+\psi_{13})(s+\psi_{14})(s+\psi_{15})(s+\psi_{16})\\
&+C_{11} s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\alpha_2)(s+\alpha_3)(s+\alpha_5)(s+\alpha_6)\\
&(s+\eta_2)(s+\eta_3)(s+\psi_1)(s+\psi_2)(s+\psi_3)(s+\psi_4)(s+\psi_5)(s+\psi_6)(s+\psi_7)(s+\psi_8)\\
&(s+\psi_{10})(s+\psi_{11})(s+\psi_{12})(s+\psi_{13})(s+\psi_{14})(s+\psi_{15})(s+\psi_{16})\\
&+C_{11} s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\alpha_2)(s+\alpha_3)(s+\alpha_5)(s+\alpha_6)\\
&(s+\eta_2)(s+\eta_3)(s+\psi_1)(s+\psi_2)(s+\psi_3)(s+\psi_4)(s+\psi_5)(s+\psi_6)(s+\psi_7)(s+\psi_8)\\
&(s+\psi_9)(s+\psi_{11})(s+\psi_{12})(s+\psi_{13})(s+\psi_{14})(s+\psi_{15})(s+\psi_{16})\\
&-C_{11} s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\alpha_2)(s+\alpha_3)(s+\alpha_5)(s+\alpha_6)\\
&(s+\eta_2)(s+\eta_3)(s+\psi_1)(s+\psi_2)(s+\psi_3)(s+\psi_4)(s+\psi_5)(s+\psi_6)(s+\psi_7)(s+\psi_8)\\
&(s+\psi_9)(s+\psi_{10})(s+\psi_{12})(s+\psi_{13})(s+\psi_{14})(s+\psi_{15})(s+\psi_{16})\\
&-C_{11} s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\alpha_2)(s+\alpha_3)(s+\alpha_5)(s+\alpha_6)\\
&(s+\eta_2)(s+\eta_3)(s+\psi_1)(s+\psi_2)(s+\psi_3)(s+\psi_4)(s+\psi_5)(s+\psi_6)(s+\psi_7)(s+\psi_8)\\
&(s+\psi_9)(s+\psi_{10})(s+\psi_{11})(s+\psi_{13})(s+\psi_{14})(s+\psi_{15})(s+\psi_{16})\\
&+C_{12} s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\alpha_2)(s+\alpha_3)(s+\alpha_5)(s+\alpha_6)\\
&(s+\eta_2)(s+\eta_3)(s+\psi_1)(s+\psi_2)(s+\psi_3)(s+\psi_4)(s+\psi_5)(s+\psi_6)(s+\psi_7)(s+\psi_8)\\
&(s+\psi_9)(s+\psi_{10})(s+\psi_{11})(s+\psi_{12})(s+\psi_{14})(s+\psi_{15})(s+\psi_{16})\\
&+C_{12} s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\alpha_2)(s+\alpha_3)(s+\alpha_5)(s+\alpha_6)\\
&(s+\eta_2)(s+\eta_3)(s+\psi_1)(s+\psi_2)(s+\psi_3)(s+\psi_4)(s+\psi_5)(s+\psi_6)(s+\psi_7)(s+\psi_8)\\
&(s+\psi_9)(s+\psi_{10})(s+\psi_{11})(s+\psi_{12})(s+\psi_{13})(s+\psi_{15})(s+\psi_{16})\\
&-C_{12} s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\alpha_2)(s+\alpha_3)(s+\alpha_5)(s+\alpha_6)\\
&(s+\eta_2)(s+\eta_3)(s+\psi_1)(s+\psi_2)(s+\psi_3)(s+\psi_4)(s+\psi_5)(s+\psi_6)(s+\psi_7)(s+\psi_8)\\
&(s+\psi_9)(s+\psi_{10})(s+\psi_{11})(s+\psi_{12})(s+\psi_{13})(s+\psi_{14})(s+\psi_{16})\\
&-C_{12} s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\alpha_2)(s+\alpha_3)(s+\alpha_5)(s+\alpha_6)\\
&(s+\eta_2)(s+\eta_3)(s+\psi_1)(s+\psi_2)(s+\psi_3)(s+\psi_4)(s+\psi_5)(s+\psi_6)(s+\psi_7)(s+\psi_8)\\
&(s+\psi_9)(s+\psi_{10})(s+\psi_{11})(s+\psi_{12})(s+\psi_{13})(s+\psi_{14})(s+\psi_{15})\\
&+C_{D0} s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\alpha_2)(s+\alpha_3)(s+\alpha_5)(s+\alpha_6)\\
&(s+\eta_2)(s+\eta_3)(s+\psi_1)(s+\psi_2)(s+\psi_3)(s+\psi_4)(s+\psi_5)(s+\psi_6)(s+\psi_7)(s+\psi_8)\\
&(s+\psi_9)(s+\psi_{10})(s+\psi_{11})(s+\psi_{12})(s+\psi_{13})(s+\psi_{14})(s+\psi_{15})(s+\psi_{16})\\
&\div\begin{bmatrix}
s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\alpha_2)(s+\alpha_3)(s+\alpha_5)(s+\alpha_6)\\
(s+\eta_2)(s+\eta_3)(s+\psi_1)(s+\psi_2)(s+\psi_3)(s+\psi_4)(s+\psi_5)(s+\psi_6)(s+\psi_7)(s+\psi_8)\\
(s+\psi_9)(s+\psi_{10})(s+\psi_{11})(s+\psi_{12})(s+\psi_{13})(s+\psi_{14})(s+\psi_{15})(s+\psi_{16})(s+k_3')
\end{bmatrix}
\end{aligned}
$$

… (C25).

Using partial fraction technique:

$$LC_D = \frac{A_{17}}{s} + \frac{A_{18}}{s+\beta_2} + \frac{A_{19}}{s+\beta_3} + \frac{A_{20}}{s+\beta_5} + \frac{A_{21}}{s+\beta_6} + \frac{A_{22}}{s+\omega_2} + \frac{A_{23}}{s+\omega_3} + \frac{A_{24}}{s+\alpha_2} + \frac{A_{25}}{s+\alpha_3}$$
$$+ \frac{A_{26}}{s+\alpha_5} + \frac{A_{27}}{s+\alpha_6} + \frac{A_{28}}{s+\eta_2} + \frac{A_{29}}{s+\eta_3} + \frac{A_{30}}{s+\psi_1} + \frac{A_{31}}{s+\psi_2} + \frac{A_{32}}{s+\psi_3} + \frac{A_{33}}{s+\psi_4} + \frac{A_{34}}{s+\psi_5}$$
$$+ \frac{A_{35}}{s+\psi_6} + \frac{A_{36}}{s+\psi_7} + \frac{A_{37}}{s+\psi_8} + \frac{A_{38}}{s+\psi_9} + \frac{A_{39}}{s+\psi_{10}} + \frac{A_{40}}{s+\psi_{11}} + \frac{A_{41}}{s+\psi_{12}} + \frac{A_{42}}{s+\psi_{13}} + \frac{A_{43}}{s+\psi_{14}}$$
$$+ \frac{A_{44}}{s+\psi_{15}} + \frac{A_{45}}{s+\psi_{16}} + \frac{A_{46}}{s+k_3'}$$

… (C26).

Taking inverse Laplace:

$$C_D = A_{17} + A_{18}e^{-\beta_2 t} + A_{19}e^{-\beta_3 t} + A_{20}e^{-\beta_5 t} + A_{21}e^{-\beta_6 t} + A_{22}e^{-\omega_2 t} + A_{23}e^{-\omega_3 t}$$
$$+ A_{24}e^{-\alpha_2 t} + A_{25}e^{-\alpha_3 t} + A_{26}e^{-\alpha_5 t} + A_{27}e^{-\alpha_6 t} + A_{28}e^{-\eta_2 t} + A_{29}e^{-\eta_3 t}$$
$$+ A_{30}e^{-\psi_1 t} + A_{31}e^{-\psi_2 t} + A_{32}e^{-\psi_3 t} + A_{33}e^{-\psi_4 t} + A_{34}e^{-\psi_5 t} + A_{35}e^{-\psi_6 t} + A_{36}e^{-\psi_7 t} + A_{37}e^{-\psi_8 t}$$
$$+ A_{38}e^{-\psi_9 t} + A_{39}e^{-\psi_{10} t} + A_{40}e^{-\psi_{11} t} + A_{41}e^{-\psi_{12} t} + A_{42}e^{-\psi_{13} t} + A_{43}e^{-\psi_{14} t} + A_{44}e^{-\psi_{15} t} + A_{45}e^{-\psi_{16} t}$$
$$+ A_{46}e^{-k_3' t}$$

… (C27).

Similar to the previous part:

$$A_{17} = \frac{C_{13} - C_1}{k_3'}$$

$$A_{18} = -\frac{C_2}{k_3' - \beta_2}$$

$$A_{19} = \frac{C_2}{k_3' - \beta_3}$$

$$A_{20} = -\frac{C_3}{k_3' - \beta_5}$$

$$A_{21} = \frac{C_3}{k_3' - \beta_6}$$

$$A_{22} = \frac{C_8 - C_4}{k_3' - \omega_2}$$

$$A_{23} = -\frac{C_8 - C_4}{k_3' - \omega_3}$$

$$A_{24} = \frac{C_9}{k_3' - \alpha_2}$$

$$A_{25} = -\frac{C_9}{k_3' - \alpha_3}$$

$$A_{26} = \frac{C_{10}}{k_3' - \alpha_5}$$

$$A_{27} = -\frac{C_{10}}{k_3' - \alpha_6}$$

$$A_{28} = \frac{C_7}{k_3' - \eta_2}$$

$$A_{29} = -\frac{C_7}{k_3' - \eta_3}$$

$$A_{30} = -\frac{C_5}{k_3' - \psi_1}$$

$$A_{31} = -\frac{C_5}{k_3' - \psi_2}$$

$$A_{32} = \frac{C_5}{k_3' - \psi_3}$$

$$A_{33} = \frac{C_5}{k_3' - \psi_4}$$

$$A_{34} = -\frac{C_6}{k_3' - \psi_5}$$

$$A_{35} = -\frac{C_6}{k_3' - \psi_6}$$

$$A_{36} = \frac{C_6}{k_3' - \psi_7}$$

$$A_{37} = \frac{C_6}{k_3' - \psi_8}$$

$$A_{38} = \frac{C_{11}}{k_3' - \psi_9}$$

$$A_{39} = \frac{C_{11}}{k_3' - \psi_{10}}$$

$$A_{40} = -\frac{C_{11}}{k_3' - \psi_{11}}$$

$$A_{41} = -\frac{C_{11}}{k_3' - \psi_{12}}$$

$$A_{42} = \frac{C_{12}}{k_3' - \psi_{13}}$$

$$A_{43} = \frac{C_{12}}{k_3' - \psi_{14}}$$

$$A_{44} = -\frac{C_{12}}{k_3' - \psi_{15}}$$

$$A_{45} = -\frac{C_{12}}{k_3' - \psi_{16}}$$

$$A_{46} = -A_{17} - A_{18} - A_{19} - A_{20} - A_{21} - A_{22} - A_{23} - A_{24} - A_{25} - A_{26} - A_{27} - A_{28}$$
$$- A_{29} - A_{30} - A_{31} - A_{32} - A_{33} - A_{34} - A_{35} - A_{36} - A_{37} - A_{38} - A_{39} - A_{40} - A_{41}$$
$$- A_{42} - A_{43} - A_{44} - A_{45} + C_{D0}$$

Substitute $A_i$, $C_i$, and $\psi_i$ into equation (C27):

$$C_D = \left( \frac{k_1' C_{T0} + k_4 C_{M0} C_{E0} - k_2 C_{D0} C_{E0}}{k_3'} \right) + \left( - \frac{k_2 C_{E0} \left( \frac{\beta_1}{\beta_3 - \beta_2} \right)}{k_3' - \beta_2} \right) e^{-\beta_2 t} + \left( \frac{k_2 C_{E0} \left( \frac{\beta_1}{\beta_3 - \beta_2} \right)}{k_3' - \beta_3} \right) e^{-\beta_3 t}$$

$$+ \left( \frac{k_2 C_{E0} \left( \frac{\beta_4}{\beta_6 - \beta_5} \right)}{k_3' - \beta_5} \right) e^{-\beta_5 t} + \left( - \frac{k_2 C_{E0} \left( \frac{\beta_4}{\beta_6 - \beta_5} \right)}{k_3' - \beta_6} \right) e^{-\beta_6 t} + \left( \frac{\left( k_4 C_{M0} - k_2 C_{D0} \right) \left( \frac{\omega_1}{\omega_3 - \omega_2} \right)}{k_3' - \omega_2} \right) e^{-\omega_2 t}$$

$$+ \left( - \frac{\left( k_4 C_{M0} - k_2 C_{D0} \right) \left( \frac{\omega_1}{\omega_3 - \omega_2} \right)}{k_3' - \omega_3} \right) e^{-\omega_3 t} + \left( \frac{k_4 C_{E0} \left( \frac{\alpha_1}{\alpha_3 - \alpha_2} \right)}{k_3' - \alpha_2} \right) e^{-\alpha_2 t} + \left( - \frac{k_4 C_{E0} \left( \frac{\alpha_1}{\alpha_3 - \alpha_2} \right)}{k_3' - \alpha_3} \right) e^{-\alpha_3 t}$$

$$+ \left( - \frac{k_4 C_{E0} \left( \frac{\alpha_4}{\alpha_6 - \alpha_5} \right)}{k_3' - \alpha_5} \right) e^{-\alpha_5 t} + \left( \frac{k_4 C_{E0} \left( \frac{\alpha_4}{\alpha_6 - \alpha_5} \right)}{k_3' - \alpha_6} \right) e^{-\alpha_6 t} + \left( \frac{k_1 \left( \frac{\eta_1}{\eta_3 - \eta_2} \right)}{k_3' - \eta_2} \right) e^{-\eta_2 t}$$

$$+ \left( - \frac{k_1 \left( \frac{\eta_1}{\eta_3 - \eta_2} \right)}{k_3' - \eta_3} \right) e^{-\eta_3 t} + \left( - \frac{k_2 \left( \frac{\beta_1}{\beta_3 - \beta_2} \right) \left( \frac{\omega_1}{\omega_3 - \omega_2} \right)}{k_3' - \left( \beta_2 + \omega_2 \right)} \right) e^{-(\beta_2 + \omega_2) t} + \left( - \frac{k_2 \left( \frac{\beta_1}{\beta_3 - \beta_2} \right) \left( \frac{\omega_1}{\omega_3 - \omega_2} \right)}{k_3' - \left( \beta_3 + \omega_3 \right)} \right) e^{-(\beta_3 + \omega_3) t}$$

$$+\left(\frac{k_2\left(\frac{\beta_1}{\beta_3-\beta_2}\right)\left(\frac{\omega_1}{\omega_3-\omega_2}\right)}{k_3'-(\beta_2+\omega_3)}\right)e^{-(\beta_2+\omega_3)t}+\left(\frac{k_2\left(\frac{\beta_1}{\beta_3-\beta_2}\right)\left(\frac{\omega_1}{\omega_3-\omega_2}\right)}{k_3'-(\beta_3+\omega_2)}\right)e^{-(\beta_3+\omega_2)t}+\left(\frac{k_2\left(\frac{\beta_4}{\beta_6-\beta_5}\right)\left(\frac{\omega_1}{\omega_3-\omega_2}\right)}{k_3'-(\beta_5+\omega_2)}\right)e^{-(\beta_5+\omega_2)t}$$

$$+\left(\frac{k_2\left(\frac{\beta_4}{\beta_6-\beta_5}\right)\left(\frac{\omega_1}{\omega_3-\omega_2}\right)}{k_3'-(\beta_6+\omega_3)}\right)e^{-(\beta_6+\omega_3)t}+\left(-\frac{k_2\left(\frac{\beta_4}{\beta_6-\beta_5}\right)\left(\frac{\omega_1}{\omega_3-\omega_2}\right)}{k_3'-(\beta_5+\omega_3)}\right)e^{-(\beta_5+\omega_3)t}+\left(-\frac{k_2\left(\frac{\beta_4}{\beta_6-\beta_5}\right)\left(\frac{\omega_1}{\omega_3-\omega_2}\right)}{k_3'-(\beta_6+\omega_2)}\right)e^{-(\beta_6+\omega_2)t}$$

$$+\left(\frac{k_4\left(\frac{\alpha_1}{\alpha_3-\alpha_2}\right)\left(\frac{\omega_1}{\omega_3-\omega_2}\right)}{k_3'-(\alpha_2+\omega_2)}\right)e^{-(\alpha_2+\omega_2)t}+\left(\frac{k_4\left(\frac{\alpha_1}{\alpha_3-\alpha_2}\right)\left(\frac{\omega_1}{\omega_3-\omega_2}\right)}{k_3'-(\alpha_3+\omega_3)}\right)e^{-(\alpha_3+\omega_3)t}+\left(-\frac{k_4\left(\frac{\alpha_1}{\alpha_3-\alpha_2}\right)\left(\frac{\omega_1}{\omega_3-\omega_2}\right)}{k_3'-(\alpha_2+\omega_3)}\right)e^{-(\alpha_2+\omega_3)t}$$

$$+\left(-\frac{k_4\left(\frac{\alpha_1}{\alpha_3-\alpha_2}\right)\left(\frac{\omega_1}{\omega_3-\omega_2}\right)}{k_3'-(\alpha_3+\omega_2)}\right)e^{-(\alpha_3+\omega_2)t}+\left(-\frac{k_4\left(\frac{\alpha_4}{\alpha_6-\alpha_5}\right)\left(\frac{\omega_1}{\omega_3-\omega_2}\right)}{k_3'-(\alpha_5+\omega_2)}\right)e^{-(\alpha_5+\omega_2)t}+\left(-\frac{k_4\left(\frac{\alpha_4}{\alpha_6-\alpha_5}\right)\left(\frac{\omega_1}{\omega_3-\omega_2}\right)}{k_3'-(\alpha_6+\omega_3)}\right)e^{-(\alpha_6+\omega_3)t}$$

$$+\left(\frac{k_4\left(\frac{\alpha_4}{\alpha_6-\alpha_5}\right)\left(\frac{\omega_1}{\omega_3-\omega_2}\right)}{k_3'-(\alpha_5+\omega_3)}\right)e^{-(\alpha_5+\omega_3)t}+\left(\frac{k_4\left(\frac{\alpha_4}{\alpha_6-\alpha_5}\right)\left(\frac{\omega_1}{\omega_3-\omega_2}\right)}{k_3'-(\alpha_6+\omega_2)}\right)e^{-(\alpha_6+\omega_2)t}$$

$$
+\left[\begin{array}{l}
-\left(\frac{k_1'C_{T0}+k_4C_{M0}C_{E0}-k_2C_{D0}C_{E0}}{k_3'}\right)+\left(\frac{k_2C_{E0}\left(\frac{\beta_1}{\beta_3-\beta_2}\right)}{k_3'-\beta_2}\right)-\left(\frac{k_2C_{E0}\left(\frac{\beta_1}{\beta_3-\beta_2}\right)}{k_3'-\beta_3}\right)-\left(\frac{k_2C_{E0}\left(\frac{\beta_4}{\beta_6-\beta_5}\right)}{k_3'-\beta_5}\right)-\left(-\frac{k_2C_{E0}\left(\frac{\beta_4}{\beta_6-\beta_5}\right)}{k_3'-\beta_6}\right)\\
-\left(\frac{\left(k_4C_{M0}-k_2C_{D0}\right)\left(\frac{\omega_1}{\omega_3-\omega_2}\right)}{k_3'-\omega_2}\right)-\left(-\frac{\left(k_4C_{M0}-k_2C_{D0}\right)\left(\frac{\omega_1}{\omega_3-\omega_2}\right)}{k_3'-\omega_3}\right)-\left(\frac{k_4C_{E0}\left(\frac{\alpha_1}{\alpha_3-\alpha_2}\right)}{k_3'-\alpha_2}\right)-\left(-\frac{k_4C_{E0}\left(\frac{\alpha_1}{\alpha_3-\alpha_2}\right)}{k_3'-\alpha_3}\right)-\left(-\frac{k_4C_{E0}\left(\frac{\alpha_4}{\alpha_6-\alpha_5}\right)}{k_3'-\alpha_5}\right)\\
-\left(\frac{k_4C_{E0}\left(\frac{\alpha_4}{\alpha_6-\alpha_5}\right)}{k_3'-\alpha_6}\right)-\left(\frac{k_1\left(\frac{\eta_1}{\eta_3-\eta_2}\right)}{k_3'-\eta_2}\right)-\left(-\frac{k_1\left(\frac{\eta_1}{\eta_3-\eta_2}\right)}{k_3'-\eta_3}\right)-\left(-\frac{k_2\left(\frac{\beta_1}{\beta_3-\beta_2}\right)\left(\frac{\omega_1}{\omega_3-\omega_2}\right)}{k_3'-\left(\beta_2+\omega_2\right)}\right)-\left(-\frac{k_2\left(\frac{\beta_1}{\beta_3-\beta_2}\right)\left(\frac{\omega_1}{\omega_3-\omega_2}\right)}{k_3'-\left(\beta_3+\omega_3\right)}\right)\\
-\left(\frac{k_2\left(\frac{\beta_1}{\beta_3-\beta_2}\right)\left(\frac{\omega_1}{\omega_3-\omega_2}\right)}{k_3'-\left(\beta_2+\omega_3\right)}\right)-\left(\frac{k_2\left(\frac{\beta_1}{\beta_3-\beta_2}\right)\left(\frac{\omega_1}{\omega_3-\omega_2}\right)}{k_3'-\left(\beta_3+\omega_2\right)}\right)-\left(\frac{k_2\left(\frac{\beta_4}{\beta_6-\beta_5}\right)\left(\frac{\omega_1}{\omega_3-\omega_2}\right)}{k_3'-\left(\beta_5+\omega_2\right)}\right)-\left(\frac{k_2\left(\frac{\beta_4}{\beta_6-\beta_5}\right)\left(\frac{\omega_1}{\omega_3-\omega_2}\right)}{k_3'-\left(\beta_6+\omega_3\right)}\right)-\left(-\frac{k_2\left(\frac{\beta_4}{\beta_6-\beta_5}\right)\left(\frac{\omega_1}{\omega_3-\omega_2}\right)}{k_3'-\left(\beta_5+\omega_3\right)}\right)\\
-\left(-\frac{k_2\left(\frac{\beta_4}{\beta_6-\beta_5}\right)\left(\frac{\omega_1}{\omega_3-\omega_2}\right)}{k_3'-\left(\beta_6+\omega_2\right)}\right)-\left(\frac{k_4\left(\frac{\alpha_1}{\alpha_3-\alpha_2}\right)\left(\frac{\omega_1}{\omega_3-\omega_2}\right)}{k_3'-\left(\alpha_2+\omega_2\right)}\right)-\left(\frac{k_4\left(\frac{\alpha_1}{\alpha_3-\alpha_2}\right)\left(\frac{\omega_1}{\omega_3-\omega_2}\right)}{k_3'-\left(\alpha_3+\omega_3\right)}\right)-\left(-\frac{k_4\left(\frac{\alpha_1}{\alpha_3-\alpha_2}\right)\left(\frac{\omega_1}{\omega_3-\omega_2}\right)}{k_3'-\left(\alpha_2+\omega_3\right)}\right)-\left(-\frac{k_4\left(\frac{\alpha_1}{\alpha_3-\alpha_2}\right)\left(\frac{\omega_1}{\omega_3-\omega_2}\right)}{k_3'-\left(\alpha_3+\omega_2\right)}\right)\\
-\left(-\frac{k_4\left(\frac{\alpha_4}{\alpha_6-\alpha_5}\right)\left(\frac{\omega_1}{\omega_3-\omega_2}\right)}{k_3'-\left(\alpha_5+\omega_2\right)}\right)-\left(-\frac{k_4\left(\frac{\alpha_4}{\alpha_6-\alpha_5}\right)\left(\frac{\omega_1}{\omega_3-\omega_2}\right)}{k_3'-\left(\alpha_6+\omega_3\right)}\right)-\left(\frac{k_4\left(\frac{\alpha_4}{\alpha_6-\alpha_5}\right)\left(\frac{\omega_1}{\omega_3-\omega_2}\right)}{k_3'-\left(\alpha_5+\omega_3\right)}\right)-\left(\frac{k_4\left(\frac{\alpha_4}{\alpha_6-\alpha_5}\right)\left(\frac{\omega_1}{\omega_3-\omega_2}\right)}{k_3'-\left(\alpha_6+\omega_2\right)}\right)+C_{D0}
\end{array}\right]e^{-k_3't}
$$

… (C28).

Equation (C28) is the solution to equation (C20). The two unknown parameters $k_3$ and $k_4$ can be evaluated by means of non-linear regression.

Determination of $k_5$ and $k_6$

Rate of concentration change of MG is rate of formation of MG in (C3) and (C6) minus the rate of disappearance of MG in (C4) and (C5):

$$\frac{dC_M}{dt} = k_3' C_D - k_4 C_M C_E - k_5' C_M + k_6 C_G C_E \quad \ldots \text{(C29)}.$$

Similar to equation (C10), glycerol can be expressed as:

$$C_G = \frac{\chi_1 \left( e^{-\chi_2 t} - e^{-\chi_3 t} \right)}{\chi_3 - \chi_2} \quad \ldots \text{(C30)}.$$

From equation (C20) and (C24):

$$k_4 C_M C_E = k_4 C_{M0} C_{E0} + C_8 \left( e^{-\omega_2 t} - e^{-\omega_3 t} \right) + C_9 \left( e^{-\alpha_2 t} - e^{-\alpha_3 t} \right) + C_{10} \left( e^{-\alpha_5 t} - e^{-\alpha_6 t} \right)$$
$$+ C_{11} \left( e^{-\psi_9 t} + e^{-\psi_{10} t} - e^{-\psi_{11} t} - e^{-\psi_{12} t} \right) + C_{12} \left( e^{-\psi_{13} t} + e^{-\psi_{14} t} - e^{-\psi_{15} t} - e^{-\psi_{16} t} \right)$$

… (C31).

Substitute (C10), (C11), C(30), and (C31) into (C29):

$$\frac{dC_M}{dt} + k_5' C_M = k_3' \left( C_{D0} + \frac{\beta_1 \left( e^{-\beta_2 t} - e^{-\beta_3 t} \right)}{\beta_3 - \beta_2} - \frac{\beta_4 \left( e^{-\beta_5 t} - e^{-\beta_6 t} \right)}{\beta_6 - \beta_5} \right)$$
$$- k_4 C_{M0} C_{E0} - C_8 \left( e^{-\omega_2 t} - e^{-\omega_3 t} \right) - C_9 \left( e^{-\alpha_2 t} - e^{-\alpha_3 t} \right) - C_{10} \left( e^{-\alpha_5 t} - e^{-\alpha_6 t} \right)$$
$$- C_{11} \left( e^{-\psi_9 t} + e^{-\psi_{10} t} - e^{-\psi_{11} t} - e^{-\psi_{12} t} \right) - C_{12} \left( e^{-\psi_{13} t} + e^{-\psi_{14} t} - e^{-\psi_{15} t} - e^{-\psi_{16} t} \right)$$
$$+ k_6 \left( \frac{\chi_1 \left( e^{-\chi_2 t} - e^{-\chi_3 t} \right)}{\chi_3 - \chi_2} \right) \left( C_{E0} + \frac{\omega_1 \left( e^{-\omega_2 t} - e^{-\omega_3 t} \right)}{\omega_3 - \omega_2} \right)$$

$$\frac{dC_M}{dt} + k_5' C_M = k_3' C_{D0} + k_3'\left(\frac{\beta_1}{\beta_3 - \beta_2}\right)\left(e^{-\beta_2 t} - e^{-\beta_3 t}\right) - k_3'\left(\frac{\beta_4}{\beta_6 - \beta_5}\right)\left(e^{-\beta_5 t} - e^{-\beta_6 t}\right)$$
$$- k_4 C_{M0} C_{E0} - C_8\left(e^{-\omega_2 t} - e^{-\omega_3 t}\right) - C_9\left(e^{-\alpha_2 t} - e^{-\alpha_3 t}\right) - C_{10}\left(e^{-\alpha_5 t} - e^{-\alpha_6 t}\right)$$
$$- C_{11}\left(e^{-\psi_9 t} + e^{-\psi_{10} t} - e^{-\psi_{11} t} - e^{-\psi_{12} t}\right) - C_{12}\left(e^{-\psi_{13} t} + e^{-\psi_{14} t} - e^{-\psi_{15} t} - e^{-\psi_{16} t}\right)$$
$$+ k_6 C_{E0}\left(\frac{\chi_1}{\chi_3 - \chi_2}\right)\left(e^{-\chi_2 t} - e^{-\chi_3 t}\right) + k_6\left(\frac{\omega_1}{\omega_3 - \omega_2}\right)\left(\frac{\chi_1}{\chi_3 - \chi_2}\right)\left(e^{-\omega_2 t} - e^{-\omega_3 t}\right)\left(e^{-\chi_2 t} - e^{-\chi_3 t}\right)$$

Next, we let

$$C_{14} = k_3'\left(\frac{\beta_1}{\beta_3 - \beta_2}\right)$$
$$C_{15} = -k_3'\left(\frac{\beta_4}{\beta_6 - \beta_5}\right)$$
$$C_{16} = k_6 C_{E0}\left(\frac{\chi_1}{\chi_3 - \chi_2}\right)$$
$$C_{17} = k_6\left(\frac{\omega_1}{\omega_3 - \omega_2}\right)\left(\frac{\chi_1}{\chi_3 - \chi_2}\right)$$
$$C_{18} = k_3' C_{D0} - k_4 C_{M0} C_{E0}$$

$$\psi_{17} = \omega_2 + \chi_2$$
$$\psi_{18} = \omega_3 + \chi_3$$
$$\psi_{19} = \omega_2 + \chi_3$$
$$\psi_{20} = \omega_3 + \chi_2$$

Then,

$$\frac{dC_M}{dt} + k_5 C_M = k_3 C_{D0} + C_{14}\left(e^{-\beta_2 t} - e^{-\beta_3 t}\right) + C_{15}\left(e^{-\beta_5 t} - e^{-\beta_6 t}\right)$$
$$- k_4 C_{M0} C_{E0} - C_8\left(e^{-\omega_2 t} - e^{-\omega_3 t}\right) - C_9\left(e^{-\alpha_2 t} - e^{-\alpha_3 t}\right) - C_{10}\left(e^{-\alpha_5 t} - e^{-\alpha_6 t}\right)$$
$$- C_{11}\left(e^{-\psi_9 t} + e^{-\psi_{10} t} - e^{-\psi_{11} t} - e^{-\psi_{12} t}\right) - C_{12}\left(e^{-\psi_{13} t} + e^{-\psi_{14} t} - e^{-\psi_{15} t} - e^{-\psi_{16} t}\right)$$
$$+ C_{16}\left(e^{-\chi_2 t} - e^{-\chi_3 t}\right) + C_{17}\left(e^{-\psi_{17} t} + e^{-\psi_{18} t} - e^{-\psi_{19} t} - e^{-\psi_{20} t}\right)$$

$$\frac{dC_M}{dt} + k_5' C_M = C_{18} + C_{14}\left(e^{-\beta_2 t} - e^{-\beta_3 t}\right) + C_{15}\left(e^{-\beta_5 t} - e^{-\beta_6 t}\right) - C_8\left(e^{-\omega_2 t} - e^{-\omega_3 t}\right)$$
$$- C_9\left(e^{-\alpha_2 t} - e^{-\alpha_3 t}\right) - C_{10}\left(e^{-\alpha_5 t} - e^{-\alpha_6 t}\right) + C_{16}\left(e^{-\chi_2 t} - e^{-\chi_3 t}\right)$$
$$- C_{11}\left(e^{-\psi_9 t} + e^{-\psi_{10} t} - e^{-\psi_{11} t} - e^{-\psi_{12} t}\right) - C_{12}\left(e^{-\psi_{13} t} + e^{-\psi_{14} t} - e^{-\psi_{15} t} - e^{-\psi_{16} t}\right)$$
$$+ C_{17}\left(e^{-\psi_{17} t} + e^{-\psi_{18} t} - e^{-\psi_{19} t} - e^{-\psi_{20} t}\right)$$

… (C32).

Taking Laplace;

$$LC_M^{'} + k_5' LC_M = C_{18} L(1) + C_{14}\left(Le^{-\beta_2 t} - Le^{-\beta_3 t}\right) + C_{15}\left(Le^{-\beta_5 t} - Le^{-\beta_6 t}\right) - C_8\left(Le^{-\omega_2 t} - Le^{-\omega_3 t}\right)$$
$$- C_9\left(Le^{-\alpha_2 t} - Le^{-\alpha_3 t}\right) - C_{10}\left(Le^{-\alpha_5 t} - Le^{-\alpha_6 t}\right) + C_{16}\left(Le^{-\chi_2 t} - Le^{-\chi_3 t}\right)$$
$$- C_{11}\left(Le^{-\psi_9 t} + Le^{-\psi_{10} t} - Le^{-\psi_{11} t} - Le^{-\psi_{12} t}\right) - C_{12}\left(Le^{-\psi_{13} t} + Le^{-\psi_{14} t} - Le^{-\psi_{15} t} - Le^{-\psi_{16} t}\right)$$
$$+ C_{17}\left(Le^{-\psi_{17} t} + Le^{-\psi_{18} t} - Le^{-\psi_{19} t} - Le^{-\psi_{20} t}\right)$$

$$LC_M^{'} + k_5' LC_M = C_{18} L(1) + C_{14}\left(Le^{-\beta_2 t} - Le^{-\beta_3 t}\right) + C_{15}\left(Le^{-\beta_5 t} - Le^{-\beta_6 t}\right) - C_8\left(Le^{-\omega_2 t} - Le^{-\omega_3 t}\right)$$
$$- C_9\left(Le^{-\alpha_2 t} - Le^{-\alpha_3 t}\right) - C_{10}\left(Le^{-\alpha_5 t} - Le^{-\alpha_6 t}\right) + C_{16}\left(Le^{-\chi_2 t} - Le^{-\chi_3 t}\right)$$
$$- C_{11}\left(Le^{-\psi_9 t} + Le^{-\psi_{10} t} - Le^{-\psi_{11} t} - Le^{-\psi_{12} t}\right) - C_{12}\left(Le^{-\psi_{13} t} + Le^{-\psi_{14} t} - Le^{-\psi_{15} t} - Le^{-\psi_{16} t}\right)$$
$$+ C_{17}\left(Le^{-\psi_{17} t} + Le^{-\psi_{18} t} - Le^{-\psi_{19} t} - Le^{-\psi_{20} t}\right)$$

$$sLC_M - C_{M0} + k_5' LC_M = \frac{C_{18}}{s} + \frac{C_{14}}{s+\beta_2} - \frac{C_{14}}{s+\beta_3} + \frac{C_{15}}{s+\beta_5} - \frac{C_{15}}{s+\beta_6} - \frac{C_8}{s+\omega_2} + \frac{C_8}{s+\omega_3}$$
$$- \frac{C_9}{s+\alpha_2} + \frac{C_9}{s+\alpha_3} - \frac{C_{10}}{s+\alpha_5} + \frac{C_{10}}{s+\alpha_6} + \frac{C_{16}}{s+\chi_2} - \frac{C_{16}}{s+\chi_3} - \frac{C_{11}}{s+\psi_9} - \frac{C_{11}}{s+\psi_{10}} + \frac{C_{11}}{s+\psi_{11}}$$
$$+ \frac{C_{11}}{s+\psi_{12}} - \frac{C_{12}}{s+\psi_{13}} - \frac{C_{12}}{s+\psi_{14}} + \frac{C_{12}}{s+\psi_{15}} + \frac{C_{12}}{s+\psi_{16}} + \frac{C_{17}}{s+\psi_{17}} + \frac{C_{17}}{s+\psi_{18}} - \frac{C_{17}}{s+\psi_{19}} - \frac{C_{17}}{s+\psi_{20}}$$

… (C33).

$$
\begin{aligned}
&LC_M = \\
&C_{18}(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\alpha_2)(s+\alpha_3)(s+\alpha_5)(s+\alpha_6)(s+\chi_2)(s+\chi_3)(s+\psi_9) \\
&(s+\psi_{10})(s+\psi_{11})(s+\psi_{12})(s+\psi_{13})(s+\psi_{14})(s+\psi_{15})(s+\psi_{16})(s+\psi_{17})(s+\psi_{18})(s+\psi_{19})(s+\psi_{20}) \\
&+ C_{14}s(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\alpha_2)(s+\alpha_3)(s+\alpha_5)(s+\alpha_6)(s+\chi_2)(s+\chi_3)(s+\psi_9) \\
&(s+\psi_{10})(s+\psi_{11})(s+\psi_{12})(s+\psi_{13})(s+\psi_{14})(s+\psi_{15})(s+\psi_{16})(s+\psi_{17})(s+\psi_{18})(s+\psi_{19})(s+\psi_{20}) \\
&- C_{14}s(s+\beta_2)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\alpha_2)(s+\alpha_3)(s+\alpha_5)(s+\alpha_6)(s+\chi_2)(s+\chi_3)(s+\psi_9) \\
&(s+\psi_{10})(s+\psi_{11})(s+\psi_{12})(s+\psi_{13})(s+\psi_{14})(s+\psi_{15})(s+\psi_{16})(s+\psi_{17})(s+\psi_{18})(s+\psi_{19})(s+\psi_{20}) \\
&+ C_{15}s(s+\beta_2)(s+\beta_3)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\alpha_2)(s+\alpha_3)(s+\alpha_5)(s+\alpha_6)(s+\chi_2)(s+\chi_3)(s+\psi_9) \\
&(s+\psi_{10})(s+\psi_{11})(s+\psi_{12})(s+\psi_{13})(s+\psi_{14})(s+\psi_{15})(s+\psi_{16})(s+\psi_{17})(s+\psi_{18})(s+\psi_{19})(s+\psi_{20}) \\
&- C_{15}s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\omega_2)(s+\omega_3)(s+\alpha_2)(s+\alpha_3)(s+\alpha_5)(s+\alpha_6)(s+\chi_2)(s+\chi_3)(s+\psi_9) \\
&(s+\psi_{10})(s+\psi_{11})(s+\psi_{12})(s+\psi_{13})(s+\psi_{14})(s+\psi_{15})(s+\psi_{16})(s+\psi_{17})(s+\psi_{18})(s+\psi_{19})(s+\psi_{20}) \\
&- C_8s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_3)(s+\alpha_2)(s+\alpha_3)(s+\alpha_5)(s+\alpha_6)(s+\chi_2)(s+\chi_3)(s+\psi_9) \\
&(s+\psi_{10})(s+\psi_{11})(s+\psi_{12})(s+\psi_{13})(s+\psi_{14})(s+\psi_{15})(s+\psi_{16})(s+\psi_{17})(s+\psi_{18})(s+\psi_{19})(s+\psi_{20}) \\
&+ C_8s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\alpha_2)(s+\alpha_3)(s+\alpha_5)(s+\alpha_6)(s+\chi_2)(s+\chi_3)(s+\psi_9) \\
&(s+\psi_{10})(s+\psi_{11})(s+\psi_{12})(s+\psi_{13})(s+\psi_{14})(s+\psi_{15})(s+\psi_{16})(s+\psi_{17})(s+\psi_{18})(s+\psi_{19})(s+\psi_{20})
\end{aligned}
$$

$$
\begin{aligned}
&- C_9 s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\alpha_3)(s+\alpha_5)(s+\alpha_6)(s+\chi_2)(s+\chi_3)(s+\psi_9)\\
&(s+\psi_{10})(s+\psi_{11})(s+\psi_{12})(s+\psi_{13})(s+\psi_{14})(s+\psi_{15})(s+\psi_{16})(s+\psi_{17})(s+\psi_{18})(s+\psi_{19})(s+\psi_{20})\\
&+ C_9 s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\alpha_2)(s+\alpha_5)(s+\alpha_6)(s+\chi_2)(s+\chi_3)(s+\psi_9)\\
&(s+\psi_{10})(s+\psi_{11})(s+\psi_{12})(s+\psi_{13})(s+\psi_{14})(s+\psi_{15})(s+\psi_{16})(s+\psi_{17})(s+\psi_{18})(s+\psi_{19})(s+\psi_{20})\\
&- C_{10} s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\alpha_2)(s+\alpha_3)(s+\alpha_6)(s+\chi_2)(s+\chi_3)(s+\psi_9)\\
&(s+\psi_{10})(s+\psi_{11})(s+\psi_{12})(s+\psi_{13})(s+\psi_{14})(s+\psi_{15})(s+\psi_{16})(s+\psi_{17})(s+\psi_{18})(s+\psi_{19})(s+\psi_{20})\\
&+ C_{10} s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\alpha_2)(s+\alpha_3)(s+\alpha_5)(s+\chi_2)(s+\chi_3)(s+\psi_9)\\
&(s+\psi_{10})(s+\psi_{11})(s+\psi_{12})(s+\psi_{13})(s+\psi_{14})(s+\psi_{15})(s+\psi_{16})(s+\psi_{17})(s+\psi_{18})(s+\psi_{19})(s+\psi_{20})\\
&+ C_{16} s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\alpha_2)(s+\alpha_3)(s+\alpha_5)(s+\alpha_6)(s+\chi_3)(s+\psi_9)\\
&(s+\psi_{10})(s+\psi_{11})(s+\psi_{12})(s+\psi_{13})(s+\psi_{14})(s+\psi_{15})(s+\psi_{16})(s+\psi_{17})(s+\psi_{18})(s+\psi_{19})(s+\psi_{20})\\
&- C_{16} s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\alpha_2)(s+\alpha_3)(s+\alpha_5)(s+\alpha_6)(s+\chi_2)(s+\psi_9)\\
&(s+\psi_{10})(s+\psi_{11})(s+\psi_{12})(s+\psi_{13})(s+\psi_{14})(s+\psi_{15})(s+\psi_{16})(s+\psi_{17})(s+\psi_{18})(s+\psi_{19})(s+\psi_{20})\\
&- C_{11} s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\alpha_2)(s+\alpha_3)(s+\alpha_5)(s+\alpha_6)(s+\chi_2)(s+\chi_3)\\
&(s+\psi_{10})(s+\psi_{11})(s+\psi_{12})(s+\psi_{13})(s+\psi_{14})(s+\psi_{15})(s+\psi_{16})(s+\psi_{17})(s+\psi_{18})(s+\psi_{19})(s+\psi_{20})\\
&- C_{11} s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\alpha_2)(s+\alpha_3)(s+\alpha_5)(s+\alpha_6)(s+\chi_2)(s+\chi_3)(s+\psi_9)\\
&(s+\psi_{11})(s+\psi_{12})(s+\psi_{13})(s+\psi_{14})(s+\psi_{15})(s+\psi_{16})(s+\psi_{17})(s+\psi_{18})(s+\psi_{19})(s+\psi_{20})\\
&+ C_{11} s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\alpha_2)(s+\alpha_3)(s+\alpha_5)(s+\alpha_6)(s+\chi_2)(s+\chi_3)(s+\psi_9)\\
&(s+\psi_{10})(s+\psi_{12})(s+\psi_{13})(s+\psi_{14})(s+\psi_{15})(s+\psi_{16})(s+\psi_{17})(s+\psi_{18})(s+\psi_{19})(s+\psi_{20})\\
&+ C_{11} s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\alpha_2)(s+\alpha_3)(s+\alpha_5)(s+\alpha_6)(s+\chi_2)(s+\chi_3)(s+\psi_9)\\
&(s+\psi_{10})(s+\psi_{11})(s+\psi_{13})(s+\psi_{14})(s+\psi_{15})(s+\psi_{16})(s+\psi_{17})(s+\psi_{18})(s+\psi_{19})(s+\psi_{20})\\
&- C_{12} s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\alpha_2)(s+\alpha_3)(s+\alpha_5)(s+\alpha_6)(s+\chi_2)(s+\chi_3)(s+\psi_9)\\
&(s+\psi_{10})(s+\psi_{11})(s+\psi_{12})(s+\psi_{14})(s+\psi_{15})(s+\psi_{16})(s+\psi_{17})(s+\psi_{18})(s+\psi_{19})(s+\psi_{20})\\
&- C_{12} s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\alpha_2)(s+\alpha_3)(s+\alpha_5)(s+\alpha_6)(s+\chi_2)(s+\chi_3)(s+\psi_9)\\
&(s+\psi_{10})(s+\psi_{11})(s+\psi_{12})(s+\psi_{13})(s+\psi_{15})(s+\psi_{16})(s+\psi_{17})(s+\psi_{18})(s+\psi_{19})(s+\psi_{20})\\
&+ C_{12} s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\alpha_2)(s+\alpha_3)(s+\alpha_5)(s+\alpha_6)(s+\chi_2)(s+\chi_3)(s+\psi_9)\\
&(s+\psi_{10})(s+\psi_{11})(s+\psi_{12})(s+\psi_{13})(s+\psi_{14})(s+\psi_{16})(s+\psi_{17})(s+\psi_{18})(s+\psi_{19})(s+\psi_{20})\\
&+ C_{12} s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\alpha_2)(s+\alpha_3)(s+\alpha_5)(s+\alpha_6)(s+\chi_2)(s+\chi_3)(s+\psi_9)\\
&(s+\psi_{10})(s+\psi_{11})(s+\psi_{12})(s+\psi_{13})(s+\psi_{14})(s+\psi_{15})(s+\psi_{17})(s+\psi_{18})(s+\psi_{19})(s+\psi_{20})\\
&+ C_{17} s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\alpha_2)(s+\alpha_3)(s+\alpha_5)(s+\alpha_6)(s+\chi_2)(s+\chi_3)(s+\psi_9)\\
&(s+\psi_{10})(s+\psi_{11})(s+\psi_{12})(s+\psi_{13})(s+\psi_{14})(s+\psi_{15})(s+\psi_{16})(s+\psi_{18})(s+\psi_{19})(s+\psi_{20})\\
&+ C_{17} s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\alpha_2)(s+\alpha_3)(s+\alpha_5)(s+\alpha_6)(s+\chi_2)(s+\chi_3)(s+\psi_9)\\
&(s+\psi_{10})(s+\psi_{11})(s+\psi_{12})(s+\psi_{13})(s+\psi_{14})(s+\psi_{15})(s+\psi_{16})(s+\psi_{17})(s+\psi_{19})(s+\psi_{20})\\
&- C_{17} s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\alpha_2)(s+\alpha_3)(s+\alpha_5)(s+\alpha_6)(s+\chi_2)(s+\chi_3)(s+\psi_9)\\
&(s+\psi_{10})(s+\psi_{11})(s+\psi_{12})(s+\psi_{13})(s+\psi_{14})(s+\psi_{15})(s+\psi_{16})(s+\psi_{17})(s+\psi_{18})(s+\psi_{20})\\
&- C_{17} s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\alpha_2)(s+\alpha_3)(s+\alpha_5)(s+\alpha_6)(s+\chi_2)(s+\chi_3)(s+\psi_9)\\
&(s+\psi_{10})(s+\psi_{11})(s+\psi_{12})(s+\psi_{13})(s+\psi_{14})(s+\psi_{15})(s+\psi_{16})(s+\psi_{17})(s+\psi_{18})(s+\psi_{19})\\
&+ C_{M0} s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\alpha_2)(s+\alpha_3)(s+\alpha_5)(s+\alpha_6)(s+\chi_2)(s+\chi_3)(s+\psi_9)\\
&(s+\psi_{10})(s+\psi_{11})(s+\psi_{12})(s+\psi_{13})(s+\psi_{14})(s+\psi_{15})(s+\psi_{16})(s+\psi_{17})(s+\psi_{18})(s+\psi_{19})(s+\psi_{20})\\
\div&\left[\begin{matrix} s(s+\beta_2)(s+\beta_3)(s+\beta_5)(s+\beta_6)(s+\omega_2)(s+\omega_3)(s+\alpha_2)(s+\alpha_3)(s+\alpha_5)(s+\alpha_6)(s+\chi_2)(s+\chi_3)(s+\psi_9)\\ (s+\psi_{10})(s+\psi_{11})(s+\psi_{12})(s+\psi_{13})(s+\psi_{14})(s+\psi_{15})(s+\psi_{16})(s+\psi_{17})(s+\psi_{18})(s+\psi_{19})(s+\psi_{20})(s+k_5') \end{matrix}\right]
\end{aligned}
$$

… (C34).

Using the partial fraction technique:

$$LC_M = \frac{A_{47}}{s} + \frac{A_{48}}{(s+\beta_2)} + \frac{A_{49}}{(s+\beta_3)} + \frac{A_{50}}{(s+\beta_5)} + \frac{A_{51}}{(s+\beta_6)} + \frac{A_{52}}{(s+\omega_2)} + \frac{A_{53}}{(s+\omega_3)} + \frac{A_{54}}{(s+\alpha_2)} + \frac{A_{55}}{(s+\alpha_3)}$$
$$+ \frac{A_{56}}{(s+\alpha_5)} + \frac{A_{57}}{(s+\alpha_6)} + \frac{A_{58}}{(s+\chi_2)} + \frac{A_{59}}{(s+\chi_3)} + \frac{A_{60}}{(s+\psi_9)} + \frac{A_{61}}{(s+\psi_{10})} + \frac{A_{62}}{(s+\psi_{11})} + \frac{A_{63}}{(s+\psi_{12})} + \frac{A_{64}}{(s+\psi_{13})}$$
$$+ \frac{A_{65}}{(s+\psi_{14})} + \frac{A_{66}}{(s+\psi_{15})} + \frac{A_{67}}{(s+\psi_{16})} + \frac{A_{68}}{(s+\psi_{17})} + \frac{A_{69}}{(s+\psi_{18})} + \frac{A_{70}}{(s+\psi_{19})} + \frac{A_{71}}{(s+\psi_{20})} + \frac{A_{72}}{(s+k_5')}$$

… (C35).

Taking the inverse Laplace:

$$C_M = A_{47} + A_{48}e^{-\beta_2 t} + A_{49}e^{-\beta_3 t} + A_{50}e^{-\beta_5 t} + A_{51}e^{-\beta_6 t} + A_{52}e^{-\omega_2 t} + A_{53}e^{-\omega_3 t} + A_{54}e^{-\alpha_2 t}$$
$$+ A_{55}e^{-\alpha_3 t} + A_{56}e^{-\alpha_5 t} + A_{57}e^{-\alpha_6 t} + A_{58}e^{-\chi_2 t} + A_{59}e^{-\chi_3 t} + A_{60}e^{-\psi_9 t} + A_{61}e^{-\psi_{10} t} + A_{62}e^{-\psi_{11} t}$$
$$+ A_{63}e^{-\psi_{12} t} + A_{64}e^{-\psi_{13} t} + A_{65}e^{-\psi_{14} t} + A_{66}e^{-\psi_{15} t} + A_{67}e^{-\psi_{16} t} + A_{68}e^{-\psi_{17} t} + A_{69}e^{-\psi_{18} t}$$
$$+ A_{70}e^{-\psi_{19} t} + A_{71}e^{-\psi_{20} t} + A_{72}e^{-k_5' t}$$

… (C36).

Similar to the previous part,

$$A_{47} = \frac{C_{18}}{k_5'}$$

$$A_{48} = \frac{C_{14}}{k_5' - \beta_2}$$

$$A_{49} = -\frac{C_{14}}{k_5' - \beta_3}$$

$$A_{50} = \frac{C_{15}}{k_5' - \beta_5}$$

$$A_{51} = -\frac{C_{15}}{k_5' - \beta_6}$$

$$A_{52} = -\frac{C_8}{k_5' - \omega_2}$$

$$A_{53} = \frac{C_8}{k_5' - \omega_3}$$

$$A_{54} = -\frac{C_9}{k_5' - \alpha_2}$$

$$A_{55} = \frac{C_9}{k_5' - \alpha_3}$$

$$A_{56} = -\frac{C_{10}}{k_5' - \alpha_5}$$

$$A_{57} = \frac{C_{10}}{k_5' - \alpha_6}$$

$$A_{58} = \frac{C_{16}}{k_5' - \chi_2}$$

$$A_{59} = -\frac{C_{16}}{k_5' - \chi_3}$$

$$A_{60} = -\frac{C_{11}}{k_5' - \psi_9}$$

$$A_{61} = -\frac{C_{11}}{k_5' - \psi_{10}}$$

$$A_{62} = \frac{C_{11}}{k_5' - \psi_{11}}$$

$$A_{63} = \frac{C_{11}}{k_5' - \psi_{12}}$$

$$A_{64} = -\frac{C_{12}}{k_5' - \psi_{13}}$$

$$A_{65} = -\frac{C_{12}}{k_5' - \psi_{14}}$$

$$A_{66} = \frac{C_{12}}{k_5' - \psi_{15}}$$

$$A_{67} = \frac{C_{12}}{k_5' - \psi_{16}}$$

$$A_{68} = \frac{C_{17}}{k_5' - \psi_{17}}$$

$$A_{69} = \frac{C_{17}}{k_5' - \psi_{18}}$$

$$A_{70} = -\frac{C_{17}}{k_5' - \psi_{19}}$$

$$A_{71} = -\frac{C_{17}}{k_5' - \psi_{20}}$$

$$A_{72} = -A_{47} - A_{48} - A_{49} - A_{50} - A_{51} - A_{52} - A_{53} - A_{54} - A_{55} - A_{56} - A_{57} - A_{58} - A_{59}$$
$$- A_{60} - A_{61} - A_{62} - A_{63} - A_{64} - A_{65} - A_{66} - A_{67} - A_{68} - A_{69} - A_{70} - A_{71} + C_{M0}$$

Substitute $A_i$, $C_i$, and $\psi_i$ into equation (C36):

$$C_M = \frac{\left(k_3' C_{D0} - k_4 C_{M0} C_{E0}\right)}{k_5'} + \frac{k_3'\left(\frac{\beta_1}{\beta_3 - \beta_2}\right)}{k_5' - \beta_2} e^{-\beta_2 t} - \frac{k_3'\left(\frac{\beta_1}{\beta_3 - \beta_2}\right)}{k_5' - \beta_3} e^{-\beta_3 t} - \frac{k_3'\left(\frac{\beta_4}{\beta_6 - \beta_5}\right)}{k_5' - \beta_5} e^{-\beta_5 t} + \frac{k_3'\left(\frac{\beta_4}{\beta_6 - \beta_5}\right)}{k_5' - \beta_6} e^{-\beta_6 t}$$

$$- \frac{k_4 C_{M0}\left(\frac{\omega_1}{\omega_3 - \omega_2}\right)}{k_5' - \omega_2} e^{-\omega_2 t} + \frac{k_4 C_{M0}\left(\frac{\omega_1}{\omega_3 - \omega_2}\right)}{k_5' - \omega_3} e^{-\omega_3 t} - \frac{k_4 C_{E0}\left(\frac{\alpha_1}{\alpha_3 - \alpha_2}\right)}{k_5' - \alpha_2} e^{-\alpha_2 t} + \frac{k_4 C_{E0}\left(\frac{\alpha_1}{\alpha_3 - \alpha_2}\right)}{k_5' - \alpha_3} e^{-\alpha_3 t} + \frac{k_4 C_{E0}\left(\frac{\alpha_4}{\alpha_6 - \alpha_5}\right)}{k_5' - \alpha_5} e^{-\alpha_5 t}$$

$$- \frac{k_4 C_{E0}\left(\frac{\alpha_4}{\alpha_6 - \alpha_5}\right)}{k_5' - \alpha_6} e^{-\alpha_6 t} + \frac{k_6 C_{E0}\left(\frac{\chi_1}{\chi_3 - \chi_2}\right)}{k_5' - \chi_2} e^{-\chi_2 t} - \frac{k_6 C_{E0}\left(\frac{\chi_1}{\chi_3 - \chi_2}\right)}{k_5' - \chi_3} e^{-\chi_3 t} - \frac{k_4\left(\frac{\alpha_1}{\alpha_3 - \alpha_2}\right)\left(\frac{\omega_1}{\omega_3 - \omega_2}\right)}{k_5' - \left(\alpha_2 + \omega_2\right)} e^{-(\alpha_2 + \omega_2)t} - \frac{k_4\left(\frac{\alpha_1}{\alpha_3 - \alpha_2}\right)\left(\frac{\omega_1}{\omega_3 - \omega_2}\right)}{k_5' - \left(\alpha_3 + \omega_3\right)} e^{-(\alpha_3 + \omega_3)t}$$

$$+ \frac{k_4\left(\frac{\alpha_1}{\alpha_3 - \alpha_2}\right)\left(\frac{\omega_1}{\omega_3 - \omega_2}\right)}{k_5' - \left(\alpha_2 + \omega_3\right)} e^{-(\alpha_2 + \omega_3)t} + \frac{k_4\left(\frac{\alpha_1}{\alpha_3 - \alpha_2}\right)\left(\frac{\omega_1}{\omega_3 - \omega_2}\right)}{k_5' - \left(\alpha_3 + \omega_2\right)} e^{-(\alpha_3 + \omega_2)t} + \frac{k_4\left(\frac{\alpha_4}{\alpha_6 - \alpha_5}\right)\left(\frac{\omega_1}{\omega_3 - \omega_2}\right)}{k_5' - \left(\alpha_5 + \omega_2\right)} e^{-(\alpha_5 + \omega_2)t} + \frac{k_4\left(\frac{\alpha_4}{\alpha_6 - \alpha_5}\right)\left(\frac{\omega_1}{\omega_3 - \omega_2}\right)}{k_5' - \left(\alpha_6 + \omega_3\right)} e^{-(\alpha_6 + \omega_3)t}$$

$$- \frac{k_4\left(\frac{\alpha_4}{\alpha_6 - \alpha_5}\right)\left(\frac{\omega_1}{\omega_3 - \omega_2}\right)}{k_5' - \left(\alpha_5 + \omega_3\right)} e^{-(\alpha_5 + \omega_3)t} - \frac{k_4\left(\frac{\alpha_4}{\alpha_6 - \alpha_5}\right)\left(\frac{\omega_1}{\omega_3 - \omega_2}\right)}{k_5' - \left(\alpha_6 + \omega_2\right)} e^{-(\alpha_6 + \omega_2)t} + \frac{k_6\left(\frac{\omega_1}{\omega_3 - \omega_2}\right)\left(\frac{\chi_1}{\chi_3 - \chi_2}\right)}{k_5' - \left(\omega_2 + \chi_2\right)} e^{-(\omega_2 + \chi_2)t} + \frac{k_6\left(\frac{\omega_1}{\omega_3 - \omega_2}\right)\left(\frac{\chi_1}{\chi_3 - \chi_2}\right)}{k_5' - \left(\omega_3 + \chi_3\right)} e^{-(\omega_3 + \chi_3)t}$$

$$- \frac{k_6\left(\frac{\omega_1}{\omega_3 - \omega_2}\right)\left(\frac{\chi_1}{\chi_3 - \chi_2}\right)}{k_5' - \left(\omega_2 + \chi_3\right)} e^{-(\omega_2 + \chi_3)t} - \frac{k_6\left(\frac{\omega_1}{\omega_3 - \omega_2}\right)\left(\frac{\chi_1}{\chi_3 - \chi_2}\right)}{k_5' - \left(\omega_3 + \chi_2\right)} e^{-(\omega_3 + \chi_2)t}$$

$$
+\left[\begin{array}{l}
-\dfrac{\left(k_3'C_{D0}-k_4C_{M0}C_{E0}\right)}{k_5'}-\dfrac{k_3'\left(\dfrac{\beta_1}{\beta_3-\beta_2}\right)}{k_5'-\beta_2}+\dfrac{k_3'\left(\dfrac{\beta_1}{\beta_3-\beta_2}\right)}{k_5'-\beta_3}+\dfrac{k_3'\left(\dfrac{\beta_4}{\beta_6-\beta_5}\right)}{k_5'-\beta_5}-\dfrac{k_3'\left(\dfrac{\beta_4}{\beta_6-\beta_5}\right)}{k_5'-\beta_6} \\
+\dfrac{k_4C_{M0}\left(\dfrac{\omega_1}{\omega_3-\omega_2}\right)}{k_5'-\omega_2}-\dfrac{k_4C_{M0}\left(\dfrac{\omega_1}{\omega_3-\omega_2}\right)}{k_5'-\omega_3}+\dfrac{k_4C_{E0}\left(\dfrac{\alpha_1}{\alpha_3-\alpha_2}\right)}{k_5'-\alpha_2}-\dfrac{k_4C_{E0}\left(\dfrac{\alpha_1}{\alpha_3-\alpha_2}\right)}{k_5'-\alpha_3}-\dfrac{k_4C_{E0}\left(\dfrac{\alpha_4}{\alpha_6-\alpha_5}\right)}{k_5'-\alpha_5} \\
+\dfrac{k_4C_{E0}\left(\dfrac{\alpha_4}{\alpha_6-\alpha_5}\right)}{k_5'-\alpha_6}-\dfrac{k_6C_{E0}\left(\dfrac{\chi_1}{\chi_3-\chi_2}\right)}{k_5'-\chi_2}+\dfrac{k_6C_{E0}\left(\dfrac{\chi_1}{\chi_3-\chi_2}\right)}{k_5'-\chi_3}+\dfrac{k_4\left(\dfrac{\alpha_1}{\alpha_3-\alpha_2}\right)\left(\dfrac{\omega_1}{\omega_3-\omega_2}\right)}{k_5'-\left(\alpha_2+\omega_2\right)}+\dfrac{k_4\left(\dfrac{\alpha_1}{\alpha_3-\alpha_2}\right)\left(\dfrac{\omega_1}{\omega_3-\omega_2}\right)}{k_5'-\left(\alpha_3+\omega_3\right)} \\
-\dfrac{k_4\left(\dfrac{\alpha_1}{\alpha_3-\alpha_2}\right)\left(\dfrac{\omega_1}{\omega_3-\omega_2}\right)}{k_5'-\left(\alpha_2+\omega_3\right)}-\dfrac{k_4\left(\dfrac{\alpha_1}{\alpha_3-\alpha_2}\right)\left(\dfrac{\omega_1}{\omega_3-\omega_2}\right)}{k_5'-\left(\alpha_3+\omega_2\right)}-\dfrac{k_4\left(\dfrac{\alpha_4}{\alpha_6-\alpha_5}\right)\left(\dfrac{\omega_1}{\omega_3-\omega_2}\right)}{k_5'-\left(\alpha_5+\omega_2\right)}-\dfrac{k_4\left(\dfrac{\alpha_4}{\alpha_6-\alpha_5}\right)\left(\dfrac{\omega_1}{\omega_3-\omega_2}\right)}{k_5'-\left(\alpha_6+\omega_3\right)} \\
+\dfrac{k_4\left(\dfrac{\alpha_4}{\alpha_6-\alpha_5}\right)\left(\dfrac{\omega_1}{\omega_3-\omega_2}\right)}{k_5'-\left(\alpha_5+\omega_3\right)}+\dfrac{k_4\left(\dfrac{\alpha_4}{\alpha_6-\alpha_5}\right)\left(\dfrac{\omega_1}{\omega_3-\omega_2}\right)}{k_5'-\left(\alpha_6+\omega_2\right)}-\dfrac{k_6\left(\dfrac{\omega_1}{\omega_3-\omega_2}\right)\left(\dfrac{\chi_1}{\chi_3-\chi_2}\right)}{k_5'-\left(\omega_2+\chi_2\right)}-\dfrac{k_6\left(\dfrac{\omega_1}{\omega_3-\omega_2}\right)\left(\dfrac{\chi_1}{\chi_3-\chi_2}\right)}{k_5'-\left(\omega_3+\chi_3\right)} \\
+\dfrac{k_6\left(\dfrac{\omega_1}{\omega_3-\omega_2}\right)\left(\dfrac{\chi_1}{\chi_3-\chi_2}\right)}{k_5'-\left(\omega_2+\chi_3\right)}+\dfrac{k_6\left(\dfrac{\omega_1}{\omega_3-\omega_2}\right)\left(\dfrac{\chi_1}{\chi_3-\chi_2}\right)}{k_5'-\left(\omega_3+\chi_2\right)}+C_{M0}
\end{array}\right]e^{-k_5't}
$$

… (C37).

Equation (C37) is the solution to equation (C29). The two unknown parameters $k_5$ and $k_6$ can be evaluated by means of non-linear regression.

## Appendix D: MATLAB programming

Equations (C19), (C28), and (C37) showed the relationship between calculated and experimental value of tri-, di-, and monoglyceride concentrations respectively, i.e., $C_i = f(E_i)$, where $C_i$ = calculated value and $E_i$ = experimental value. The MATLAB program was written in order to compute rate constants for each particular step of the alkali-catalyzed transesterification of fryer grease based on these equations. Non-linear regression was used to determine the rate constants by minimizing the standard error of estimate ($S_{C \cdot E}$ or SEE) or the root-mean-square of residuals for N data points.

$$S_{C \cdot E} = \sqrt{\frac{\sum_{N} (C_i - E_i)^2}{N}} \quad \ldots \text{(D1)}$$

The program is composed of preliminary programs in which the constant $\alpha_i$, $\beta_i$, $\omega_i$, $\eta_i$, and $\chi_i$ were calculated and the main programs which yield the rate constants of each step. Table D1 shows each program's name and its function.

Table D1: Program name and its function used in MATLAB

| Program name | Function |
|---|---|
| Input | Stores experimental results |
| Ini_guess | Stores initial guess |
| PfitT[1] | Calculates error between experimental value and calculated value based on equation (C21) |
| PfitT_plot* | Calculates $\eta_i$ |
| PfitD* | Calculates error between experimental value and calculated value based on equation (C10) |
| PfitD_plot* | Calculates $\beta_i$ |
| PfitM* | Calculates error between experimental value and calculated value based on equation (C22) |
| PfitM_plot* | Calculates $\alpha_i$ |
| PfitE* | Calculates error between experimental value and calculated value based on equation (C11) |
| PfitE_plot* | Calculates $\omega_i$ |
| PfitG* | Calculates error between experimental value and calculated value based on equation (C30) |
| PfitG_plot* | Calculates $\chi_i$ |
| FitT[2] | Calculates error between experimental value and calculated value based on equation (C19) |
| FitT_main† | Calculates $k_1$ and $k_2$ |
| FitD† | Calculates error between experimental value and calculated value based on equation (C28) |
| FitD_main† | Calculates $k_3$ and $k_4$ |
| FitM† | Calculates error between experimental value and calculated value based on equation (C37) |
| FitM_main† | Calculates $k_5$ and $k_6$ |

[1] Preliminary program
[2] Main program

## Input

```
tt=[0 1 2 3 4 5];
T=10*[0.552309635
0.327564609
0.213651542
0.16583058
0.141586802
0.129792162];

td=[0 1 2 3 4 5];
D=10*[0.135935714
0.165998821
0.147674219
0.133781533
0.125214885
0.120244012];

tm=[0 1 2 3 4 5];
M=10*[0.017829597
0.07780995
0.103129713
0.115175368
0.116548331
0.112934706];

te=[0 1 2 3 4 5];
E=10*[0.19453626
0.730478319
1.078568166
1.238889663
1.339869661
1.398416643];

tg=[0 1 2 3 4 5];
G=10*[0
0.134701566
0.241619473
0.291287466
0.322724929
0.343104067];
```

---

## Ini_guess

```
%initial guess value for prelim fitting
%For TG
TI=[27 .5 .2];


%For DG
DI=[1 0.03 .4 11 .5 .006];



%For MG
MI=[16 1.63 .07 5 0.4 0.3];
```

```
%For ES
EI=[30 .1 .3];


%For GL
GI=[15   0.0619    2.5];
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%
%initial guess value
%For TG (k1,k2)
KTI=[.5 0];


%For DG (k3,k4)
KDI=[1.55 0.072];


%For MG (k5,k6)
KMI=[5 0.15];
```

## PfitT

```
function errT=PFITT(n)

%Input data
run Input


for i=1:length(tt)
    TCAL(i)=n(1)*(exp(-n(2)*tt(i))-exp(-n(3)*tt(i)))/(n(3)-n(2))+T(1)
    TCAL_err(i)=(TCAL(i)-T(i))^2
end

errT=sqrt((sum(TCAL_err))/length(tt));
```

## PfitT_plot

```
run Input
run ini_guess

n=fminsearch(@PFITT,[TI(1),TI(2),TI(3)])

%standard error of estimate
for i=1:length(tt)
    TCAL(i)=n(1)*(exp(-n(2)*tt(i))-exp(-n(3)*tt(i)))/(n(3)-n(2))+T(1)
    TCAL_err(i)=(TCAL(i)-T(i))^2
end

errT=sqrt((sum(TCAL_err))/length(tt));

%standard deviation
```

```
mean_TG=sum(T)/length(tt)
for i=1:length(tt)
    d(i)=T(i)-mean_TG
    ds(i)=(d(i))^2
end
s=sqrt((sum(ds))/length(tt))


%measure of correction (r^2)
rs=1-(errT^2)/(s^2)


%graphical fitting
tau=linspace(0,tt(length(tt)),100)
CALT=n(1)*(exp(-n(2)*tau)-exp(-n(3)*tau))/(n(3)-n(2))+T(1)

plot(tt,T,'ro',tau,CALT,'b-');


legend('experimental results', 'calculated resulted')
xlabel('time(min)')
ylabel('concentration(dmol/L)')


n
correlation_coefficient=sqrt(rs)
```

---

**PfitD**

```
function errD=PFITD(b)

%Input data
run Input


for i=1:length(td)
    DCAL(i)=b(1)*(exp(-b(2)*td(i))-exp(-b(3)*td(i)))/(b(3)-b(2))...
        -b(4)*(exp(-b(5)*td(i))-exp(-b(6)*td(i)))/(b(6)-b(5))+D(1)
    DCAL_err(i)=(DCAL(i)-D(i))^2
end

errD=sqrt((sum(DCAL_err))/length(td));
```

---

**PfitD_plot**

```
run Input
run ini_guess


b=fminsearch(@PFITD,[DI(1),DI(2),DI(3),DI(4),DI(5),DI(6)])

%standard error of estimate
for i=1:length(td)
    DCAL(i)=b(1)*(exp(-b(2)*td(i))-exp(-b(3)*td(i)))/(b(3)-b(2))...
```

```
        -b(4)*(exp(-b(5)*td(i))-exp(-b(6)*td(i)))/(b(6)-b(5))+D(1)
    DCAL_err(i)=(DCAL(i)-D(i))^2
end

errD=sqrt((sum(DCAL_err))/length(td));

%standard deviation
mean_DG=sum(D)/length(td)
for i=1:length(td)
    d(i)=D(i)-mean_DG
    ds(i)=(d(i))^2
end
s=sqrt((sum(ds))/length(td))


%measure of correction (r^2)
rs=1-(errD^2)/(s^2)


%graphical fitting
tau=linspace(0,td(length(td)),100)
CAL=b(1)*(exp(-b(2)*tau)-exp(-b(3)*tau))/(b(3)-b(2))...
        -b(4)*(exp(-b(5)*tau)-exp(-b(6)*tau))/(b(6)-b(5))+D(1)

plot(td,D,'ro',tau,CAL,'b-');


legend('experimental results', 'calculated resulted')
xlabel('time(min)')
ylabel('concentration(dmol/L)')


b
correlation_coefficient=sqrt(rs)
```

## PfitM

```
function errM=PFITM(a)

%Input data
run Input


for i=1:length(tm)
    MCAL(i)=a(1)*(exp(-a(2)*tm(i))-exp(-a(3)*tm(i)))/(a(3)-a(2))...
        -a(4)*(exp(-a(5)*tm(i))-exp(-a(6)*tm(i)))/(a(6)-a(5))+M(1)
    MCAL_err(i)=(MCAL(i)-M(i))^2
end
errM=sqrt((sum(MCAL_err))/length(tm))
```

## PfitM_plot

```
run Input
run ini_guess

a=fminsearch(@PFITM,[MI(1),MI(2),MI(3),MI(4),MI(5),MI(6)])

%standard error of estimate
for i=1:length(tm)
    MCAL(i)=a(1)*(exp(-a(2)*tm(i))-exp(-a(3)*tm(i)))/(a(3)-a(2))...
        -a(4)*(exp(-a(5)*tm(i))-exp(-a(6)*tm(i)))/(a(6)-a(5))+M(1)
    MCAL_err(i)=(MCAL(i)-M(i))^2
end
errM=sqrt((sum(MCAL_err))/length(tm))


%standard deviation
mean_MG=sum(M)/length(tm)
for i=1:length(tm)
    d(i)=M(i)-mean_MG
    ds(i)=(d(i))^2
end
s=sqrt((sum(ds))/length(tm))


%measure of correction (r^2)
rs=1-(errM^2)/(s^2)


%graphical fitting
tau=linspace(0,tm(length(tm)),100)
CALM=a(1)*(exp(-a(2)*tau)-exp(-a(3)*tau))/(a(3)-a(2))...
        -a(4)*(exp(-a(5)*tau)-exp(-a(6)*tau))/(a(6)-a(5))+M(1)
plot(tm,M,'ro',tau,CALM,'b-');

legend('experimental results', 'calculated resulted')
xlabel('time(min)')
ylabel('concentration(dmol/L)')

a
correlation_coefficient=sqrt(rs)
```

---

## PfitE

```
function errE=PFITE(w)

%Input data
run Input


for i=1:length(te)
    ECAL(i)=w(1)*(exp(-w(2)*te(i))-exp(-w(3)*te(i)))/(w(3)-w(2))+E(1);
    ECAL_err(i)=(ECAL(i)-E(i))^2
end
```

```
errE=sqrt((sum(ECAL_err))/length(te))
```

## PfitE_plot

```
run Input
run ini_guess

w=fminsearch(@PFITE,[EI(1),EI(2),EI(3)])

%standard error of estimate
for i=1:length(te)
    ECAL(i)=w(1)*(exp(-w(2)*te(i))-exp(-w(3)*te(i)))/(w(3)-w(2))+E(1);
    ECAL_err(i)=(ECAL(i)-E(i))^2
end
errE=sqrt((sum(ECAL_err))/length(te))


%standard deviation
mean_ES=sum(E)/length(te)
for i=1:length(te)
    d(i)=E(i)-mean_ES
    ds(i)=(d(i))^2
end
s=sqrt((sum(ds))/length(te))


%measure of correction (r^2)
rs=1-(errE^2)/(s^2)


%graphical fitting
tau=linspace(0,te(length(te)),100)
CALE=w(1)*(exp(-w(2)*tau)-exp(-w(3)*tau))/(w(3)-w(2))+E(1)

plot(te,E,'ro',tau,CALE,'b-');

legend('experimental results', 'calculated resulted')
xlabel('time(min)')
ylabel('concentration(dmol/L)')

w
correlation_coefficient=sqrt(rs)
```

## PfitG

```
function errG=PFITG(x)

%Input data
run Input


for i=1:length(tg)
```

```
    GCAL(i)=x(1)*(exp(-x(2)*tg(i))-exp(-x(3)*tg(i)))/(x(3)-x(2))
    GCAL_err(i)=(GCAL(i)-G(i))^2
end
errG=sqrt((sum(GCAL_err))/length(tg))
```

## PfitG_plot

```
run Input
run ini_guess

x=fminsearch(@PFITG,[GI(1),GI(2),GI(3)])

%standard error of estimate
for i=1:length(tg)
    GCAL(i)=x(1)*(exp(-x(2)*tg(i))-exp(-x(3)*tg(i)))/(x(3)-x(2))
    GCAL_err(i)=(GCAL(i)-G(i))^2
end
errG=sqrt((sum(GCAL_err))/length(tg))

%standard deviation
mean_GL=sum(G)/length(tg)
for i=1:length(tg)
    d(i)=G(i)-mean_GL
    ds(i)=(d(i))^2
end
s=sqrt((sum(ds))/length(tg))


%measure of correction (r^2)
rs=1-(errG^2)/(s^2)


%graphical fitting
tau=linspace(0,tg(length(tg)),100)
CALG=x(1)*(exp(-x(2)*tau)-exp(-x(3)*tau))/(x(3)-x(2))

plot(tg,G,'ro',tau,CALG,'b-');

legend('experimental results', 'calculated resulted')
xlabel('time(min)')
ylabel('concentration(dmol/L)')


x
correlation_coefficient=sqrt(rs)
```

**FitT**

```
function errTG=FITT(kt)

run Input
b=load('bData.m');
w=load('wData.m');

C(1)=kt(2)*D(1)*E(1)
C(2)=kt(2)*E(1)*(b(1)/(b(3)-b(2)))
C(3)=-kt(2)*E(1)*(b(4)/(b(6)-b(5)))
C(4)=kt(2)*D(1)*(w(1)/(w(3)-w(2)))
C(5)=kt(2)*(b(1)/(b(3)-b(2)))*(w(1)/(w(3)-w(2)))
C(6)=-kt(2)*(b(4)/(b(6)-b(5)))*(w(1)/(w(3)-w(2)))

phe(1)=b(2)+w(2)
phe(2)=b(3)+w(3)
phe(3)=b(2)+w(3)
phe(4)=b(3)+w(2)
phe(5)=b(5)+w(2)
phe(6)=b(6)+w(3)
phe(7)=b(5)+w(3)
phe(8)=b(6)+w(2)

A(1)=C(1)/kt(1)
A(2)=C(2)/(kt(1)-b(2))
A(3)=-C(2)/(kt(1)-b(3))
A(4)=C(3)/(kt(1)-b(5))
A(5)=-C(3)/(kt(1)-b(6))
A(6)=C(4)/(kt(1)-w(2))
A(7)=-C(4)/(kt(1)-w(3))
A(8)=C(5)/(kt(1)-phe(1))
A(9)=C(5)/(kt(1)-phe(2))
A(10)=-C(5)/(kt(1)-phe(3))
A(11)=-C(5)/(kt(1)-phe(4))
A(12)=C(6)/(kt(1)-phe(5))
A(13)=C(6)/(kt(1)-phe(6))
A(14)=-C(6)/(kt(1)-phe(7))
A(15)=-C(6)/(kt(1)-phe(8))
A(16)=-A(1)-A(2)-A(3)-A(4)-A(5)-A(6)-A(7)-A(8)-A(9) ...
    -A(10)-A(11)-A(12)-A(13)-A(14)-A(15)+T(1)


CT=zeros(1,length(tt))
for i=1:length(tt)
    CT(i)=A(1)+A(2)*exp(-b(2)*tt(i)) ...
        +A(3)*exp(-b(3)*tt(i)) ...
        +A(4)*exp(-b(5)*tt(i)) ...
        +A(5)*exp(-b(6)*tt(i)) ...
        +A(6)*exp(-w(2)*tt(i)) ...
        +A(7)*exp(-w(3)*tt(i)) ...
        +A(8)*exp(-phe(1)*tt(i)) ...
        +A(9)*exp(-phe(2)*tt(i)) ...
        +A(10)*exp(-phe(3)*tt(i)) ...
        +A(11)*exp(-phe(4)*tt(i)) ...
        +A(12)*exp(-phe(5)*tt(i)) ...
```

```
        +A(13)*exp(-phe(6)*tt(i)) ...
        +A(14)*exp(-phe(7)*tt(i)) ...
        +A(15)*exp(-phe(8)*tt(i)) ...
        +A(16)*exp(-kt(1)*tt(i))
    PerrTG(i)=(CT(i)-T(i))^2
end
errTG=sqrt((sum(PerrTG))/length(tt))
```

---

**FitT_main**

```
run Input
run ini_guess

fb1=fopen('bData.m','wt');
b=fminsearch(@PFITD,[DI(1),DI(2),DI(3),DI(4),DI(5),DI(6)]);
fprintf(fb1,'%f \t',b);
fclose(fb1);

fw1=fopen('wData.m','wt');
w=fminsearch(@PFITE,[EI(1),EI(2),EI(3)]);
fprintf(fw1,'%f \t',w);
fclose(fw1);

fkt1=fopen('ktData.m','wt');
kt=fminsearch(@FITT,[KTI(1),KTI(2)]);
fprintf(fkt1,'%f \t',kt);
fclose(fkt1);

fC1=fopen('CData.m','wt');
C(1)=kt(2)*D(1)*E(1)
C(2)=kt(2)*E(1)*(b(1)/(b(3)-b(2)))
C(3)=-kt(2)*E(1)*(b(4)/(b(6)-b(5)))
C(4)=kt(2)*D(1)*(w(1)/(w(3)-w(2)))
C(5)=kt(2)*(b(1)/(b(3)-b(2)))*(w(1)/(w(3)-w(2)))
C(6)=-kt(2)*(b(4)/(b(6)-b(5)))*(w(1)/(w(3)-w(2)))
fprintf(fC1,'%f \t',C);
fclose(fC1);

fphe1=fopen('pheData.m','wt');
phe(1)=b(2)+w(2)
phe(2)=b(3)+w(3)
phe(3)=b(2)+w(3)
phe(4)=b(3)+w(2)
phe(5)=b(5)+w(2)
phe(6)=b(6)+w(3)
phe(7)=b(5)+w(3)
phe(8)=b(6)+w(2)
fprintf(fphe1,'%f \t',phe);
fclose(fphe1);

fA1=fopen('AData.m','wt');
A(1)=C(1)/kt(1)
A(2)=C(2)/(kt(1)-b(2))
A(3)=-C(2)/(kt(1)-b(3))
A(4)=C(3)/(kt(1)-b(5))
```

```
A(5)=-C(3)/(kt(1)-b(6))
A(6)=C(4)/(kt(1)-w(2))
A(7)=-C(4)/(kt(1)-w(3))
A(8)=C(5)/(kt(1)-phe(1))
A(9)=C(5)/(kt(1)-phe(2))
A(10)=-C(5)/(kt(1)-phe(3))
A(11)=-C(5)/(kt(1)-phe(4))
A(12)=C(6)/(kt(1)-phe(5))
A(13)=C(6)/(kt(1)-phe(6))
A(14)=-C(6)/(kt(1)-phe(7))
A(15)=-C(6)/(kt(1)-phe(8))
A(16)=-A(1)-A(2)-A(3)-A(4)-A(5)-A(6)-A(7)-A(8)-A(9) ...
    -A(10)-A(11)-A(12)-A(13)-A(14)-A(15)+T(1)
fprintf(fA1,'%f \t',A);
fclose(fA1);


%standard error of estimate
CT=zeros(1,length(tt))
for i=1:length(tt)
    CT(i)=A(1)+A(2)*exp(-b(2)*tt(i)) ...
        +A(3)*exp(-b(3)*tt(i)) ...
        +A(4)*exp(-b(5)*tt(i)) ...
        +A(5)*exp(-b(6)*tt(i)) ...
        +A(6)*exp(-w(2)*tt(i)) ...
        +A(7)*exp(-w(3)*tt(i)) ...
        +A(8)*exp(-phe(1)*tt(i)) ...
        +A(9)*exp(-phe(2)*tt(i)) ...
        +A(10)*exp(-phe(3)*tt(i)) ...
        +A(11)*exp(-phe(4)*tt(i)) ...
        +A(12)*exp(-phe(5)*tt(i)) ...
        +A(13)*exp(-phe(6)*tt(i)) ...
        +A(14)*exp(-phe(7)*tt(i)) ...
        +A(15)*exp(-phe(8)*tt(i)) ...
        +A(16)*exp(-kt(1)*tt(i))
    PerrTG(i)=(CT(i)-T(i))^2

end
errTG=sqrt((sum(PerrTG))/length(tt))


%standard deviation
mean_TG=sum(T)/length(tt)
for i=1:length(tt)
    d(i)=T(i)-mean_TG
    ds(i)=(d(i))^2
end
s=sqrt((sum(ds))/length(tt))


%measure of correction (r^2)
rs=1-(errTG^2)/(s^2)

%graphical fitting
tau=linspace(0,tt(length(tt)),100)
CALTG=A(1)+A(2)*exp(-b(2)*tau) ...
        +A(3)*exp(-b(3)*tau) ...
```

```
        +A(4)*exp(-b(5)*tau) ...
        +A(5)*exp(-b(6)*tau) ...
        +A(6)*exp(-w(2)*tau) ...
        +A(7)*exp(-w(3)*tau) ...
        +A(8)*exp(-phe(1)*tau) ...
        +A(9)*exp(-phe(2)*tau) ...
        +A(10)*exp(-phe(3)*tau) ...
        +A(11)*exp(-phe(4)*tau) ...
        +A(12)*exp(-phe(5)*tau) ...
        +A(13)*exp(-phe(6)*tau) ...
        +A(14)*exp(-phe(7)*tau) ...
        +A(15)*exp(-phe(8)*tau) ...
        +A(16)*exp(-kt(1)*tau)

plot(tt,T,'ro',tau,CALTG,'b-');

legend('experimental results', 'calculated resulted')
xlabel('time(min)')
ylabel('concentration(dmol/L)')


rate_constant_k1k2=kt
correlation_coefficient=sqrt(rs)
```

---

**FitD**

```
function errDG=FITD(kd)

%Input data
run Input
b=load('bData.m')
w=load('wData.m')
n=load('nData.m')
a=load('aData.m')
kt=load('ktData.m');

C(1)=kt(2)*D(1)*E(1)
C(2)=kt(2)*E(1)*(b(1)/(b(3)-b(2)))
C(3)=-kt(2)*E(1)*(b(4)/(b(6)-b(5)))
C(4)=kt(2)*D(1)*(w(1)/(w(3)-w(2)))
C(5)=kt(2)*(b(1)/(b(3)-b(2)))*(w(1)/(w(3)-w(2)))
C(6)=-kt(2)*(b(4)/(b(6)-b(5)))*(w(1)/(w(3)-w(2)))
C(7)=kt(1)*(n(1)/(n(3)-n(2)))
C(8)=kd(2)*M(1)*(w(1)/(w(3)-w(2)))
C(9)=kd(2)*E(1)*(a(1)/(a(3)-a(2)))
C(10)=-kd(2)*E(1)*(a(4)/(a(6)-a(5)))
C(11)=kd(2)*(a(1)/(a(3)-a(2)))*(w(1)/(w(3)-w(2)))
C(12)=-kd(2)*(a(4)/(a(6)-a(5)))*(w(1)/(w(3)-w(2)))
C(13)=kt(1)*T(1)+kd(2)*M(1)*E(1)

phe(1)=b(2)+w(2)
phe(2)=b(3)+w(3)
phe(3)=b(2)+w(3)
phe(4)=b(3)+w(2)
phe(5)=b(5)+w(2)
```

```
phe(6)=b(6)+w(3)
phe(7)=b(5)+w(3)
phe(8)=b(6)+w(2)
phe(9)=a(2)+w(2);
phe(10)=a(3)+w(3);
phe(11)=a(2)+w(3);
phe(12)=a(3)+w(2);
phe(13)=a(5)+w(2);
phe(14)=a(6)+w(3);
phe(15)=a(5)+w(3);
phe(16)=a(6)+w(2);

A(1)=C(1)/kt(1)
A(2)=C(2)/(kt(1)-b(2))
A(3)=-C(2)/(kt(1)-b(3))
A(4)=C(3)/(kt(1)-b(5))
A(5)=-C(3)/(kt(1)-b(6))
A(6)=C(4)/(kt(1)-w(2))
A(7)=-C(4)/(kt(1)-w(3))
A(8)=C(5)/(kt(1)-phe(1))
A(9)=C(5)/(kt(1)-phe(2))
A(10)=-C(5)/(kt(1)-phe(3))
A(11)=-C(5)/(kt(1)-phe(4))
A(12)=C(6)/(kt(1)-phe(5))
A(13)=C(6)/(kt(1)-phe(6))
A(14)=-C(6)/(kt(1)-phe(7))
A(15)=-C(6)/(kt(1)-phe(8))
A(16)=-A(1)-A(2)-A(3)-A(4)-A(5)-A(6)-A(7)-A(8)-A(9) ...
    -A(10)-A(11)-A(12)-A(13)-A(14)-A(15)+T(1)
A(17)=(C(13)-C(1))/kd(1);
A(18)=-C(2)/(kd(1)-b(2));
A(19)=C(2)/(kd(1)-b(3));
A(20)=-C(3)/(kd(1)-b(5));
A(21)=C(3)/(kd(1)-b(6));
A(22)=(C(8)-C(4))/(kd(1)-w(2));
A(23)=-(C(8)-C(4))/(kd(1)-w(3));
A(24)=C(9)/(kd(1)-a(2));
A(25)=-C(9)/(kd(1)-a(3));
A(26)=C(10)/(kd(1)-a(5));
A(27)=-C(10)/(kd(1)-a(6));
A(28)=C(7)/(kd(1)-n(2));
A(29)=-C(7)/(kd(1)-n(3));
A(30)=-C(5)/(kd(1)-phe(1));
A(31)=-C(5)/(kd(1)-phe(2));
A(32)=C(5)/(kd(1)-phe(3));
A(33)=C(5)/(kd(1)-phe(4));
A(34)=-C(6)/(kd(1)-phe(5));
A(35)=-C(6)/(kd(1)-phe(6));
A(36)=C(6)/(kd(1)-phe(7));
A(37)=C(6)/(kd(1)-phe(8));
A(38)=C(11)/(kd(1)-phe(9));
A(39)=C(11)/(kd(1)-phe(10));
A(40)=-C(11)/(kd(1)-phe(11));
A(41)=-C(11)/(kd(1)-phe(12));
A(42)=C(12)/(kd(1)-phe(13));
A(43)=C(12)/(kd(1)-phe(14));
A(44)=-C(12)/(kd(1)-phe(15));
```

```
A(45)=-C(12)/(kd(1)-phe(16));
A(46)=-A(17)-A(18)-A(19)-A(20)-A(21)-A(22)-A(23)-A(24) ...
    -A(25)-A(26)-A(27)-A(28)-A(29)-A(30)-A(31)-A(32) ...
    -A(33)-A(34)-A(35)-A(36)-A(37)-A(38)-A(39)-A(40) ...
    -A(41)-A(42)-A(43)-A(44)-A(45)+D(1)

CD=zeros(1,length(td))
for i=1:length(td)

    CD(i)=A(17)+A(18)*exp(-b(2)*td(i)) ...
        +A(19)*exp(-b(3)*td(i)) ...
        +A(20)*exp(-b(5)*td(i)) ...
        +A(21)*exp(-b(6)*td(i)) ...
        +A(22)*exp(-w(2)*td(i)) ...
        +A(23)*exp(-w(3)*td(i)) ...
        +A(24)*exp(-a(2)*td(i)) ...
        +A(25)*exp(-a(3)*td(i)) ...
        +A(26)*exp(-a(5)*td(i)) ...
        +A(27)*exp(-a(6)*td(i)) ...
        +A(28)*exp(-n(2)*td(i)) ...
        +A(29)*exp(-n(3)*td(i)) ...
        +A(30)*exp(-phe(1)*td(i)) ...
        +A(31)*exp(-phe(2)*td(i)) ...
        +A(32)*exp(-phe(3)*td(i)) ...
        +A(33)*exp(-phe(4)*td(i)) ...
        +A(34)*exp(-phe(5)*td(i)) ...
        +A(35)*exp(-phe(6)*td(i)) ...
        +A(36)*exp(-phe(7)*td(i)) ...
        +A(37)*exp(-phe(8)*td(i)) ...
        +A(38)*exp(-phe(9)*td(i)) ...
        +A(39)*exp(-phe(10)*td(i)) ...
        +A(40)*exp(-phe(11)*td(i)) ...
        +A(41)*exp(-phe(12)*td(i)) ...
        +A(42)*exp(-phe(13)*td(i)) ...
        +A(43)*exp(-phe(14)*td(i)) ...
        +A(44)*exp(-phe(15)*td(i)) ...
        +A(45)*exp(-phe(16)*td(i)) ...
        +A(46)*exp(-kd(1)*td(i))
    PerrDG(i)=(CD(i)-D(i))^2
end
errDG=sqrt((sum(PerrDG))/length(td))
```

## FitD_main

```
run Input
run ini_guess
b=load('bData.m');
w=load('wData.m');
kt=load('ktData.m');

fn1=fopen('nData.m','wt');
n=fminsearch(@PFITT,[TI(1),TI(2),TI(3)]);
fprintf(fn1,'%f \t',n);
fclose(fn1);
```

```
fa1=fopen('aData.m','wt');
a=fminsearch(@PFITM,[MI(1),MI(2),MI(3),MI(4),MI(5),MI(6)]);
fprintf(fa1,'%f \t',a);
fclose(fa1);

fkd1=fopen('kdData.m','wt');
kd=fminsearch(@FITD,[KDI(1),KDI(2)]);
fprintf(fkd1,'%f \t',kd);
fclose(fkd1);

C(1)=kt(2)*D(1)*E(1)
C(2)=kt(2)*E(1)*(b(1)/(b(3)-b(2)))
C(3)=-kt(2)*E(1)*(b(4)/(b(6)-b(5)))
C(4)=kt(2)*D(1)*(w(1)/(w(3)-w(2)))
C(5)=kt(2)*(b(1)/(b(3)-b(2)))*(w(1)/(w(3)-w(2)))
C(6)=-kt(2)*(b(4)/(b(6)-b(5)))*(w(1)/(w(3)-w(2)))
C(7)=kt(1)*(n(1)/(n(3)-n(2)))
C(8)=kd(2)*M(1)*(w(1)/(w(3)-w(2)))
C(9)=kd(2)*E(1)*(a(1)/(a(3)-a(2)))
C(10)=-kd(2)*E(1)*(a(4)/(a(6)-a(5)))
C(11)=kd(2)*(a(1)/(a(3)-a(2)))*(w(1)/(w(3)-w(2)))
C(12)=-kd(2)*(a(4)/(a(6)-a(5)))*(w(1)/(w(3)-w(2)))
C(13)=kt(1)*T(1)+kd(2)*M(1)*E(1)

phe(1)=b(2)+w(2)
phe(2)=b(3)+w(3)
phe(3)=b(2)+w(3)
phe(4)=b(3)+w(2)
phe(5)=b(5)+w(2)
phe(6)=b(6)+w(3)
phe(7)=b(5)+w(3)
phe(8)=b(6)+w(2)
phe(9)=a(2)+w(2);
phe(10)=a(3)+w(3);
phe(11)=a(2)+w(3);
phe(12)=a(3)+w(2);
phe(13)=a(5)+w(2);
phe(14)=a(6)+w(3);
phe(15)=a(5)+w(3);
phe(16)=a(6)+w(2);

A(1)=C(1)/kt(1)
A(2)=C(2)/(kt(1)-b(2))
A(3)=-C(2)/(kt(1)-b(3))
A(4)=C(3)/(kt(1)-b(5))
A(5)=-C(3)/(kt(1)-b(6))
A(6)=C(4)/(kt(1)-w(2))
A(7)=-C(4)/(kt(1)-w(3))
A(8)=C(5)/(kt(1)-phe(1))
A(9)=C(5)/(kt(1)-phe(2))
A(10)=-C(5)/(kt(1)-phe(3))
A(11)=-C(5)/(kt(1)-phe(4))
A(12)=C(6)/(kt(1)-phe(5))
A(13)=C(6)/(kt(1)-phe(6))
A(14)=-C(6)/(kt(1)-phe(7))
A(15)=-C(6)/(kt(1)-phe(8))
A(16)=-A(1)-A(2)-A(3)-A(4)-A(5)-A(6)-A(7)-A(8)-A(9) ...
```

```
    -A(10)-A(11)-A(12)-A(13)-A(14)-A(15)+T(1)
A(17)=(C(13)-C(1))/kd(1);
A(18)=-C(2)/(kd(1)-b(2));
A(19)=C(2)/(kd(1)-b(3));
A(20)=-C(3)/(kd(1)-b(5));
A(21)=C(3)/(kd(1)-b(6));
A(22)=(C(8)-C(4))/(kd(1)-w(2));
A(23)=-(C(8)-C(4))/(kd(1)-w(3));
A(24)=C(9)/(kd(1)-a(2));
A(25)=-C(9)/(kd(1)-a(3));
A(26)=C(10)/(kd(1)-a(5));
A(27)=-C(10)/(kd(1)-a(6));
A(28)=C(7)/(kd(1)-n(2));
A(29)=-C(7)/(kd(1)-n(3));
A(30)=-C(5)/(kd(1)-phe(1));
A(31)=-C(5)/(kd(1)-phe(2));
A(32)=C(5)/(kd(1)-phe(3));
A(33)=C(5)/(kd(1)-phe(4));
A(34)=-C(6)/(kd(1)-phe(5));
A(35)=-C(6)/(kd(1)-phe(6));
A(36)=C(6)/(kd(1)-phe(7));
A(37)=C(6)/(kd(1)-phe(8));
A(38)=C(11)/(kd(1)-phe(9));
A(39)=C(11)/(kd(1)-phe(10));
A(40)=-C(11)/(kd(1)-phe(11));
A(41)=-C(11)/(kd(1)-phe(12));
A(42)=C(12)/(kd(1)-phe(13));
A(43)=C(12)/(kd(1)-phe(14));
A(44)=-C(12)/(kd(1)-phe(15));
A(45)=-C(12)/(kd(1)-phe(16));
A(46)=-A(17)-A(18)-A(19)-A(20)-A(21)-A(22)-A(23)-A(24) ...
    -A(25)-A(26)-A(27)-A(28)-A(29)-A(30)-A(31)-A(32) ...
    -A(33)-A(34)-A(35)-A(36)-A(37)-A(38)-A(39)-A(40) ...
    -A(41)-A(42)-A(43)-A(44)-A(45)+D(1)

%standard error of estimate
CD=zeros(1,length(td))
for i=1:length(td)
    CD(i)=A(17)+A(18)*exp(-b(2)*td(i)) ...
        +A(19)*exp(-b(3)*td(i)) ...
        +A(20)*exp(-b(5)*td(i)) ...
        +A(21)*exp(-b(6)*td(i)) ...
        +A(22)*exp(-w(2)*td(i)) ...
        +A(23)*exp(-w(3)*td(i)) ...
        +A(24)*exp(-a(2)*td(i)) ...
        +A(25)*exp(-a(3)*td(i)) ...
        +A(26)*exp(-a(5)*td(i)) ...
        +A(27)*exp(-a(6)*td(i)) ...
        +A(28)*exp(-n(2)*td(i)) ...
        +A(29)*exp(-n(3)*td(i)) ...
        +A(30)*exp(-phe(1)*td(i)) ...
        +A(31)*exp(-phe(2)*td(i)) ...
        +A(32)*exp(-phe(3)*td(i)) ...
        +A(33)*exp(-phe(4)*td(i)) ...
        +A(34)*exp(-phe(5)*td(i)) ...
        +A(35)*exp(-phe(6)*td(i)) ...
        +A(36)*exp(-phe(7)*td(i)) ...
```

```
        +A(37)*exp(-phe(8)*td(i)) ...
        +A(38)*exp(-phe(9)*td(i)) ...
        +A(39)*exp(-phe(10)*td(i)) ...
        +A(40)*exp(-phe(11)*td(i)) ...
        +A(41)*exp(-phe(12)*td(i)) ...
        +A(42)*exp(-phe(13)*td(i)) ...
        +A(43)*exp(-phe(14)*td(i)) ...
        +A(44)*exp(-phe(15)*td(i)) ...
        +A(45)*exp(-phe(16)*td(i)) ...
        +A(46)*exp(-kd(1)*td(i))
    PerrDG(i)=(CD(i)-D(i))^2
end
errDG=sqrt((sum(PerrDG))/length(td))

%standard deviation
mean_DG=sum(D)/length(td)
for i=1:length(td)
    d(i)=D(i)-mean_DG
    ds(i)=(d(i))^2
end
s=sqrt((sum(ds))/length(td))

%measure of correction (r^2)
rs=1-(errDG^2)/(s^2)

%graphical fitting
tau=linspace(0,td(length(td)),100)
CALDG=A(17)+A(18)*exp(-b(2)*tau) ...
        +A(19)*exp(-b(3)*tau) ...
        +A(20)*exp(-b(5)*tau) ...
        +A(21)*exp(-b(6)*tau) ...
        +A(22)*exp(-w(2)*tau) ...
        +A(23)*exp(-w(3)*tau) ...
        +A(24)*exp(-a(2)*tau) ...
        +A(25)*exp(-a(3)*tau) ...
        +A(26)*exp(-a(5)*tau) ...
        +A(27)*exp(-a(6)*tau) ...
        +A(28)*exp(-n(2)*tau) ...
        +A(29)*exp(-n(3)*tau) ...
        +A(30)*exp(-phe(1)*tau) ...
        +A(31)*exp(-phe(2)*tau) ...
        +A(32)*exp(-phe(3)*tau) ...
        +A(33)*exp(-phe(4)*tau) ...
        +A(34)*exp(-phe(5)*tau) ...
        +A(35)*exp(-phe(6)*tau) ...
        +A(36)*exp(-phe(7)*tau) ...
        +A(37)*exp(-phe(8)*tau) ...
        +A(38)*exp(-phe(9)*tau) ...
        +A(39)*exp(-phe(10)*tau) ...
        +A(40)*exp(-phe(11)*tau) ...
        +A(41)*exp(-phe(12)*tau) ...
        +A(42)*exp(-phe(13)*tau) ...
        +A(43)*exp(-phe(14)*tau) ...
        +A(44)*exp(-phe(15)*tau) ...
        +A(45)*exp(-phe(16)*tau) ...
        +A(46)*exp(-kd(1)*tau)
```

```
plot(td,D,'ro',tau,CALDG,'b-');

legend('experimental results', 'calculated resulted')
xlabel('time(min)')
ylabel('concentration(dmol/L)')

rate_constant_k3k4=kd
correlation_coefficient=sqrt(rs)
```

## FitM

```
function errMG=FITM(km)

%Input data
run Input
b=load('bData.m');
w=load('wData.m');
n=load('nData.m');
x=load('xData.m');
a=load('aData.m');
kt=load('ktData.m');
kd=load('kdData.m');

C(1)=kt(2)*D(1)*E(1)
C(2)=kt(2)*E(1)*(b(1)/(b(3)-b(2)))
C(3)=-kt(2)*E(1)*(b(4)/(b(6)-b(5)))
C(4)=kt(2)*D(1)*(w(1)/(w(3)-w(2)))
C(5)=kt(2)*(b(1)/(b(3)-b(2)))*(w(1)/(w(3)-w(2)))
C(6)=-kt(2)*(b(4)/(b(6)-b(5)))*(w(1)/(w(3)-w(2)))
C(7)=kt(1)*(n(1)/(n(3)-n(2)))
C(8)=kd(2)*M(1)*(w(1)/(w(3)-w(2)))
C(9)=kd(2)*E(1)*(a(1)/(a(3)-a(2)))
C(10)=-kd(2)*E(1)*(a(4)/(a(6)-a(5)))
C(11)=kd(2)*(a(1)/(a(3)-a(2)))*(w(1)/(w(3)-w(2)))
C(12)=-kd(2)*(a(4)/(a(6)-a(5)))*(w(1)/(w(3)-w(2)))
C(13)=kt(1)*T(1)+kd(2)*M(1)*E(1)
C(14)=kd(1)*(b(1)/(b(3)-b(2)))
C(15)=-kd(1)*(b(4)/(b(6)-b(5)))
C(16)=km(2)*E(1)*(x(1)/(x(3)-x(2)))
C(17)=km(2)*(w(1)/(w(3)-w(2)))*(x(1)/(x(3)-x(2)))
C(18)=kd(1)*D(1)-kd(2)*M(1)*E(1)

phe(1)=b(2)+w(2)
phe(2)=b(3)+w(3)
phe(3)=b(2)+w(3)
phe(4)=b(3)+w(2)
phe(5)=b(5)+w(2)
phe(6)=b(6)+w(3)
phe(7)=b(5)+w(3)
phe(8)=b(6)+w(2)
phe(9)=a(2)+w(2);
phe(10)=a(3)+w(3);
phe(11)=a(2)+w(3);
phe(12)=a(3)+w(2);
phe(13)=a(5)+w(2);
```

```
phe(14)=a(6)+w(3);
phe(15)=a(5)+w(3);
phe(16)=a(6)+w(2);
phe(17)=w(2)+x(2);
phe(18)=w(3)+x(3);
phe(19)=w(2)+x(3);
phe(20)=w(3)+x(2);


A(1)=C(1)/kt(1)
A(2)=C(2)/(kt(1)-b(2))
A(3)=-C(2)/(kt(1)-b(3))
A(4)=C(3)/(kt(1)-b(5))
A(5)=-C(3)/(kt(1)-b(6))
A(6)=C(4)/(kt(1)-w(2))
A(7)=-C(4)/(kt(1)-w(3))
A(8)=C(5)/(kt(1)-phe(1))
A(9)=C(5)/(kt(1)-phe(2))
A(10)=-C(5)/(kt(1)-phe(3))
A(11)=-C(5)/(kt(1)-phe(4))
A(12)=C(6)/(kt(1)-phe(5))
A(13)=C(6)/(kt(1)-phe(6))
A(14)=-C(6)/(kt(1)-phe(7))
A(15)=-C(6)/(kt(1)-phe(8))
A(16)=-A(1)-A(2)-A(3)-A(4)-A(5)-A(6)-A(7)-A(8)-A(9) ...
    -A(10)-A(11)-A(12)-A(13)-A(14)-A(15)+T(1)
A(17)=(C(13)-C(1))/kd(1);
A(18)=-C(2)/(kd(1)-b(2));
A(19)=C(2)/(kd(1)-b(3));
A(20)=-C(3)/(kd(1)-b(5));
A(21)=C(3)/(kd(1)-b(6));
A(22)=(C(8)-C(4))/(kd(1)-w(2));
A(23)=-(C(8)-C(4))/(kd(1)-w(3));
A(24)=C(9)/(kd(1)-a(2));
A(25)=-C(9)/(kd(1)-a(3));
A(26)=C(10)/(kd(1)-a(5));
A(27)=-C(10)/(kd(1)-a(6));
A(28)=C(7)/(kd(1)-n(2));
A(29)=-C(7)/(kd(1)-n(3));
A(30)=-C(5)/(kd(1)-phe(1));
A(31)=-C(5)/(kd(1)-phe(2));
A(32)=C(5)/(kd(1)-phe(3));
A(33)=C(5)/(kd(1)-phe(4));
A(34)=-C(6)/(kd(1)-phe(5));
A(35)=-C(6)/(kd(1)-phe(6));
A(36)=C(6)/(kd(1)-phe(7));
A(37)=C(6)/(kd(1)-phe(8));
A(38)=C(11)/(kd(1)-phe(9));
A(39)=C(11)/(kd(1)-phe(10));
A(40)=-C(11)/(kd(1)-phe(11));
A(41)=-C(11)/(kd(1)-phe(12));
A(42)=C(12)/(kd(1)-phe(13));
A(43)=C(12)/(kd(1)-phe(14));
A(44)=-C(12)/(kd(1)-phe(15));
A(45)=-C(12)/(kd(1)-phe(16));
A(46)=-A(17)-A(18)-A(19)-A(20)-A(21)-A(22)-A(23)-A(24) ...
    -A(25)-A(26)-A(27)-A(28)-A(29)-A(30)-A(31)-A(32) ...
```

```
    -A(33)-A(34)-A(35)-A(36)-A(37)-A(38)-A(39)-A(40) ...
    -A(41)-A(42)-A(43)-A(44)-A(45)+D(1)
A(47)=C(18)/km(1);
A(48)=C(14)/(km(1)-b(2));
A(49)=-C(14)/(km(1)-b(3));
A(50)=C(15)/(km(1)-b(5));
A(51)=-C(15)/(km(1)-b(6));
A(52)=-C(8)/(km(1)-w(2));
A(53)=C(8)/(km(1)-w(3));
A(54)=-C(9)/(km(1)-a(2));
A(55)=C(9)/(km(1)-a(3));
A(56)=-C(10)/(km(1)-a(5));
A(57)=C(10)/(km(1)-a(6));
A(58)=C(16)/(km(1)-x(2));
A(59)=-C(16)/(km(1)-x(3));
A(60)=-C(11)/(km(1)-phe(9));
A(61)=-C(11)/(km(1)-phe(10));
A(62)=C(11)/(km(1)-phe(11));
A(63)=C(11)/(km(1)-phe(12));
A(64)=-C(12)/(km(1)-phe(13));
A(65)=-C(12)/(km(1)-phe(14));
A(66)=C(12)/(km(1)-phe(15));
A(67)=C(12)/(km(1)-phe(16));
A(68)=C(17)/(km(1)-phe(17));
A(69)=C(17)/(km(1)-phe(18));
A(70)=-C(17)/(km(1)-phe(19));
A(71)=-C(17)/(km(1)-phe(20));
A(72)=-A(47)-A(48)-A(49)-A(50)-A(51)-A(52)-A(53)-A(54)-A(55) ...
    -A(56)-A(57)-A(58)-A(59)-A(60)-A(61)-A(62)-A(63)-A(64) ...
    -A(65)-A(66)-A(67)-A(68)-A(69)-A(70)-A(71)+M(1);

CM=zeros(1,length(tm))
for i=1:length(tm)
    CM(i)=A(47)+A(48)*exp(-b(2)*tm(i)) ...
        +A(49)*exp(-b(3)*tm(i)) ...
        +A(50)*exp(-b(5)*tm(i)) ...
        +A(51)*exp(-b(6)*tm(i)) ...
        +A(52)*exp(-w(2)*tm(i)) ...
        +A(53)*exp(-w(3)*tm(i)) ...
        +A(54)*exp(-a(2)*tm(i)) ...
        +A(55)*exp(-a(3)*tm(i)) ...
        +A(56)*exp(-a(5)*tm(i)) ...
        +A(57)*exp(-a(6)*tm(i)) ...
        +A(58)*exp(-x(2)*tm(i)) ...
        +A(59)*exp(-x(3)*tm(i)) ...
        +A(60)*exp(-phe(9)*tm(i)) ...
        +A(61)*exp(-phe(10)*tm(i)) ...
        +A(62)*exp(-phe(11)*tm(i)) ...
        +A(63)*exp(-phe(12)*tm(i)) ...
        +A(64)*exp(-phe(13)*tm(i)) ...
        +A(65)*exp(-phe(14)*tm(i)) ...
        +A(66)*exp(-phe(15)*tm(i)) ...
        +A(67)*exp(-phe(16)*tm(i)) ...
        +A(68)*exp(-phe(17)*tm(i)) ...
        +A(69)*exp(-phe(18)*tm(i)) ...
        +A(70)*exp(-phe(19)*tm(i)) ...
        +A(71)*exp(-phe(20)*tm(i)) ...
```

```
        +A(72)*exp(-km(1)*tm(i))
    PerrMG(i)=(CM(i)-M(i))^2
end
errMG=sqrt((sum(PerrMG))/length(tm))
```

---

## FitM_main

```
run Input
run ini_guess
b=load('bData.m');
w=load('wData.m');
n=load('nData.m');
a=load('aData.m');
kt=load('ktData.m');
kd=load('kdData.m');

fx1=fopen('xData.m','wt');
x=fminsearch(@PFITG,[GI(1),GI(2),GI(3)]);
fprintf(fx1,'%f \t',x);
fclose(fx1);

fkm1=fopen('kmData.m','wt');
km=fminsearch(@FITM,[KMI(1),KMI(2)]);
fprintf(fkm1,'%f \t',km);
fclose(fkm1);

C(1)=kt(2)*D(1)*E(1)
C(2)=kt(2)*E(1)*(b(1)/(b(3)-b(2)))
C(3)=-kt(2)*E(1)*(b(4)/(b(6)-b(5)))
C(4)=kt(2)*D(1)*(w(1)/(w(3)-w(2)))
C(5)=kt(2)*(b(1)/(b(3)-b(2)))*(w(1)/(w(3)-w(2)))
C(6)=-kt(2)*(b(4)/(b(6)-b(5)))*(w(1)/(w(3)-w(2)))
C(7)=kt(1)*(n(1)/(n(3)-n(2)))
C(8)=kd(2)*M(1)*(w(1)/(w(3)-w(2)))
C(9)=kd(2)*E(1)*(a(1)/(a(3)-a(2)))
C(10)=-kd(2)*E(1)*(a(4)/(a(6)-a(5)))
C(11)=kd(2)*(a(1)/(a(3)-a(2)))*(w(1)/(w(3)-w(2)))
C(12)=-kd(2)*(a(4)/(a(6)-a(5)))*(w(1)/(w(3)-w(2)))
C(13)=kt(1)*T(1)+kd(2)*M(1)*E(1)
C(14)=kd(1)*(b(1)/(b(3)-b(2)))
C(15)=-kd(1)*(b(4)/(b(6)-b(5)))
C(16)=km(2)*E(1)*(x(1)/(x(3)-x(2)))
C(17)=km(2)*(w(1)/(w(3)-w(2)))*(x(1)/(x(3)-x(2)))
C(18)=kd(1)*D(1)-kd(2)*M(1)*E(1)

phe(1)=b(2)+w(2)
phe(2)=b(3)+w(3)
phe(3)=b(2)+w(3)
phe(4)=b(3)+w(2)

phe(5)=b(5)+w(2)
phe(6)=b(6)+w(3)
phe(7)=b(5)+w(3)
phe(8)=b(6)+w(2)
phe(9)=a(2)+w(2);
```

```
phe(10)=a(3)+w(3);
phe(11)=a(2)+w(3);
phe(12)=a(3)+w(2);
phe(13)=a(5)+w(2);
phe(14)=a(6)+w(3);
phe(15)=a(5)+w(3);
phe(16)=a(6)+w(2);
phe(17)=w(2)+x(2);
phe(18)=w(3)+x(3);
phe(19)=w(2)+x(3);
phe(20)=w(3)+x(2);

A(1)=C(1)/kt(1)
A(2)=C(2)/(kt(1)-b(2))
A(3)=-C(2)/(kt(1)-b(3))
A(4)=C(3)/(kt(1)-b(5))
A(5)=-C(3)/(kt(1)-b(6))
A(6)=C(4)/(kt(1)-w(2))
A(7)=-C(4)/(kt(1)-w(3))
A(8)=C(5)/(kt(1)-phe(1))
A(9)=C(5)/(kt(1)-phe(2))
A(10)=-C(5)/(kt(1)-phe(3))
A(11)=-C(5)/(kt(1)-phe(4))
A(12)=C(6)/(kt(1)-phe(5))
A(13)=C(6)/(kt(1)-phe(6))
A(14)=-C(6)/(kt(1)-phe(7))
A(15)=-C(6)/(kt(1)-phe(8))
A(16)=-A(1)-A(2)-A(3)-A(4)-A(5)-A(6)-A(7)-A(8)-A(9) ...
    -A(10)-A(11)-A(12)-A(13)-A(14)-A(15)+T(1)
A(17)=(C(13)-C(1))/kd(1);
A(18)=-C(2)/(kd(1)-b(2));
A(19)=C(2)/(kd(1)-b(3));
A(20)=-C(3)/(kd(1)-b(5));
A(21)=C(3)/(kd(1)-b(6));
A(22)=(C(8)-C(4))/(kd(1)-w(2));
A(23)=-(C(8)-C(4))/(kd(1)-w(3));
A(24)=C(9)/(kd(1)-a(2));
A(25)=-C(9)/(kd(1)-a(3));
A(26)=C(10)/(kd(1)-a(5));
A(27)=-C(10)/(kd(1)-a(6));
A(28)=C(7)/(kd(1)-n(2));
A(29)=-C(7)/(kd(1)-n(3));
A(30)=-C(5)/(kd(1)-phe(1));
A(31)=-C(5)/(kd(1)-phe(2));
A(32)=C(5)/(kd(1)-phe(3));
A(33)=C(5)/(kd(1)-phe(4));
A(34)=-C(6)/(kd(1)-phe(5));
A(35)=-C(6)/(kd(1)-phe(6));
A(36)=C(6)/(kd(1)-phe(7));
A(37)=C(6)/(kd(1)-phe(8));
A(38)=C(11)/(kd(1)-phe(9));
A(39)=C(11)/(kd(1)-phe(10));
A(40)=-C(11)/(kd(1)-phe(11));
A(41)=-C(11)/(kd(1)-phe(12));
A(42)=C(12)/(kd(1)-phe(13));
A(43)=C(12)/(kd(1)-phe(14));
A(44)=-C(12)/(kd(1)-phe(15));
```

```
A(45)=-C(12)/(kd(1)-phe(16));
A(46)=-A(17)-A(18)-A(19)-A(20)-A(21)-A(22)-A(23)-A(24) ...
    -A(25)-A(26)-A(27)-A(28)-A(29)-A(30)-A(31)-A(32) ...
    -A(33)-A(34)-A(35)-A(36)-A(37)-A(38)-A(39)-A(40) ...
    -A(41)-A(42)-A(43)-A(44)-A(45)+D(1)
A(47)=C(18)/km(1);
A(48)=C(14)/(km(1)-b(2));
A(49)=-C(14)/(km(1)-b(3));
A(50)=C(15)/(km(1)-b(5));
A(51)=-C(15)/(km(1)-b(6));
A(52)=-C(8)/(km(1)-w(2));
A(53)=C(8)/(km(1)-w(3));
A(54)=-C(9)/(km(1)-a(2));
A(55)=C(9)/(km(1)-a(3));
A(56)=-C(10)/(km(1)-a(5));
A(57)=C(10)/(km(1)-a(6));
A(58)=C(16)/(km(1)-x(2));
A(59)=-C(16)/(km(1)-x(3));
A(60)=-C(11)/(km(1)-phe(9));
A(61)=-C(11)/(km(1)-phe(10));
A(62)=C(11)/(km(1)-phe(11));
A(63)=C(11)/(km(1)-phe(12));
A(64)=-C(12)/(km(1)-phe(13));
A(65)=-C(12)/(km(1)-phe(14));
A(66)=C(12)/(km(1)-phe(15));
A(67)=C(12)/(km(1)-phe(16));
A(68)=C(17)/(km(1)-phe(17));
A(69)=C(17)/(km(1)-phe(18));
A(70)=-C(17)/(km(1)-phe(19));
A(71)=-C(17)/(km(1)-phe(20));
A(72)=-A(47)-A(48)-A(49)-A(50)-A(51)-A(52)-A(53)-A(54)-A(55) ...
    -A(56)-A(57)-A(58)-A(59)-A(60)-A(61)-A(62)-A(63)-A(64) ...
    -A(65)-A(66)-A(67)-A(68)-A(69)-A(70)-A(71)+M(1);

%standard error of estimate
CM=zeros(1,length(tm))
for i=1:length(tm)
    CM(i)=A(47)+A(48)*exp(-b(2)*tm(i)) ...
        +A(49)*exp(-b(3)*tm(i)) ...
        +A(50)*exp(-b(5)*tm(i)) ...
        +A(51)*exp(-b(6)*tm(i)) ...
        +A(52)*exp(-w(2)*tm(i)) ...
        +A(53)*exp(-w(3)*tm(i)) ...
        +A(54)*exp(-a(2)*tm(i)) ...
        +A(55)*exp(-a(3)*tm(i)) ...
        +A(56)*exp(-a(5)*tm(i)) ...
        +A(57)*exp(-a(6)*tm(i)) ...
        +A(58)*exp(-x(2)*tm(i)) ...
        +A(59)*exp(-x(3)*tm(i)) ...
        +A(60)*exp(-phe(9)*tm(i)) ...
        +A(61)*exp(-phe(10)*tm(i)) ...
        +A(62)*exp(-phe(11)*tm(i)) ...
        +A(63)*exp(-phe(12)*tm(i)) ...
        +A(64)*exp(-phe(13)*tm(i)) ...
        +A(65)*exp(-phe(14)*tm(i)) ...
        +A(66)*exp(-phe(15)*tm(i)) ...
        +A(67)*exp(-phe(16)*tm(i)) ...
```

```
        +A(68)*exp(-phe(17)*tm(i)) ...
        +A(69)*exp(-phe(18)*tm(i)) ...
        +A(70)*exp(-phe(19)*tm(i)) ...
        +A(71)*exp(-phe(20)*tm(i)) ...
        +A(72)*exp(-km(1)*tm(i))
    PerrMG(i)=(CM(i)-M(i))^2
end
errMG=sqrt((sum(PerrMG))/length(tm))

%standard deviation
mean_MG=sum(M)/length(tm)
for i=1:length(tm)
    d(i)=M(i)-mean_MG
    ds(i)=(d(i))^2
end
s=sqrt((sum(ds))/length(tm))

%measure of correction (r^2)
rs=1-(errMG^2)/(s^2)

%graphical fitting
tau=linspace(0,tm(length(tm)),100)
CALMG=A(47)+A(48)*exp(-b(2)*tau) ...
        +A(49)*exp(-b(3)*tau) ...
        +A(50)*exp(-b(5)*tau) ...
        +A(51)*exp(-b(6)*tau) ...
        +A(52)*exp(-w(2)*tau) ...
        +A(53)*exp(-w(3)*tau) ...
        +A(54)*exp(-a(2)*tau) ...
        +A(55)*exp(-a(3)*tau) ...
        +A(56)*exp(-a(5)*tau) ...
        +A(57)*exp(-a(6)*tau) ...
        +A(58)*exp(-x(2)*tau) ...
        +A(59)*exp(-x(3)*tau) ...
        +A(60)*exp(-phe(9)*tau) ...
        +A(61)*exp(-phe(10)*tau) ...
        +A(62)*exp(-phe(11)*tau) ...
        +A(63)*exp(-phe(12)*tau) ...
        +A(64)*exp(-phe(13)*tau) ...
        +A(65)*exp(-phe(14)*tau) ...
        +A(66)*exp(-phe(15)*tau) ...
        +A(67)*exp(-phe(16)*tau) ...
        +A(68)*exp(-phe(17)*tau) ...
        +A(69)*exp(-phe(18)*tau) ...
        +A(70)*exp(-phe(19)*tau) ...
        +A(71)*exp(-phe(20)*tau) ...
        +A(72)*exp(-km(1)*tau)

plot(tm,M,'ro',tau,CALMG,'b-');
legend('experimental results', 'calculated resulted')
xlabel('time(min)')
ylabel('concentration(dmol/L)')

rate_constant_k5k6=km
correlation_coefficient=sqrt(rs)
```

# Appendix E: Properties of kerosene as a reference fuel in lubricity test

Table E1. Properties of the kerosene base fuel

| Fuel property | Value |
|---|---|
| Viscosity @40$^0$C | 1.33 mm$^2$/s |
| Density @15$^0$C | 0.775 g/ml |
| Acid value | 0.2 mgKOH/g |
| Heating value | 44.32 MJ/kg |
| Lubricity number | 0.689 |

Appendix F: Selected kinetic data

Table F1: Kinetic data for alkali-catalyzed transesterification of fryer grease using 0.5% KOH, 6:1 alcohol to oil molar ratio at 30 $^{o}$C

| Time [min] | Concentration [dmol/L] | | | | |
|---|---|---|---|---|---|
| | Triglyceride | Diglyceride | Monoglyceride | Methyl ester | Glycerol |
| 0.0 | 6.57719 | 1.62370 | 0.21583 | 2.36274 | 0 |
| 0.5 | 5.66585 | 1.81407 | 0.43785 | 4.41803 | 0.49894 |
| 1.0 | 4.89503 | 1.96790 | 0.61905 | 6.17943 | 0.93473 |
| 1.5 | 4.41876 | 2.01809 | 0.77954 | 7.30334 | 1.20034 |
| 2.0 | 3.92439 | 1.98242 | 0.91901 | 8.68646 | 1.59090 |
| 3.0 | 3.25993 | 1.93177 | 1.07240 | 10.46644 | 2.15262 |
| 4.0 | 2.81580 | 1.84261 | 1.14755 | 11.75679 | 2.61076 |
| 5.0 | 2.63535 | 1.76390 | 1.17107 | 12.69034 | 2.84640 |
| 6.0 | 2.32913 | 1.69419 | 1.16864 | 13.35686 | 3.22474 |
| 7.0 | 2.19850 | 1.64057 | 1.15113 | 13.85819 | 3.42653 |
| 8.0 | 2.10903 | 1.59806 | 1.12677 | 14.24039 | 3.58285 |
| 9.0 | 2.04622 | 1.56419 | 1.09945 | 14.54077 | 3.70686 |
| 10.0 | 2.00064 | 1.53684 | 1.07114 | 14.78502 | 3.80809 |

Table F2: Kinetic data for alkali-catalyzed transesterification of fryer grease using 0.5% KOH, 6:1 alcohol to oil molar ratio at 40 $^{o}$C

| Time [min] | Concentration [dmol/L] | | | | |
|---|---|---|---|---|---|
| | Triglyceride | Diglyceride | Monoglyceride | Methyl ester | Glycerol |
| 0.0 | 6.59275 | 1.62262 | 0.21283 | 2.32212 | 0 |
| 0.5 | 5.11580 | 1.93344 | 0.58141 | 5.63767 | 0.79755 |
| 1.0 | 3.91004 | 1.98148 | 0.92879 | 8.71950 | 1.60789 |
| 1.5 | 3.00022 | 1.89462 | 1.13667 | 11.36822 | 2.39670 |
| 2.0 | 2.55029 | 1.76274 | 1.23103 | 12.87454 | 2.88414 |
| 3.0 | 1.97947 | 1.59691 | 1.37481 | 14.78825 | 3.47701 |
| 4.0 | 1.69008 | 1.49465 | 1.39120 | 15.99362 | 3.85227 |
| 5.0 | 1.54929 | 1.43532 | 1.34807 | 16.69248 | 4.09553 |
| 6.0 | 1.47815 | 1.39431 | 1.27608 | 17.10810 | 4.27967 |
| 7.0 | 1.43967 | 1.35914 | 1.19285 | 17.36539 | 4.43654 |
| 8.0 | 1.41649 | 1.32412 | 1.10835 | 17.53417 | 4.57925 |
| 9.0 | 1.40046 | 1.28659 | 1.02786 | 17.65358 | 4.71329 |
| 10.0 | 1.42660 | 1.24652 | 0.94931 | 17.65128 | 4.80577 |

Table F3: Kinetic data for alkali-catalyzed transesterification of fryer grease using 0.5% KOH, 6:1 alcohol to oil molar ratio at 50 $^{o}$C

| Time [min] | Concentration [dmol/L] | | | | |
|---|---|---|---|---|---|
| | Triglyceride | Diglyceride | Monoglyceride | Methyl ester | Glycerol |
| 0.0 | 6.56364 | 1.62655 | 0.21315 | 2.40047 | 0 |
| 0.5 | 4.91990 | 1.95845 | 0.63154 | 6.10993 | 0.89344 |
| 1.0 | 3.28311 | 1.94621 | 1.14306 | 10.40758 | 2.03094 |
| 1.5 | 2.46197 | 1.72255 | 1.30876 | 13.12889 | 2.91004 |
| 2.0 | 2.11447 | 1.59571 | 1.36214 | 14.36818 | 3.33101 |
| 3.0 | 1.62011 | 1.46148 | 1.39922 | 16.24423 | 3.92253 |
| 4.0 | 1.41367 | 1.35573 | 1.30122 | 17.27499 | 4.33270 |
| 5.0 | 1.32552 | 1.27159 | 1.15824 | 17.82326 | 4.64798 |
| 6.0 | 1.28411 | 1.22742 | 1.04404 | 18.13188 | 4.84776 |
| 7.0 | 1.26118 | 1.18173 | 0.94174 | 18.32153 | 5.01868 |
| 8.0 | 1.24554 | 1.14055 | 0.86613 | 18.45220 | 5.15112 |
| 9.0 | 1.23277 | 1.10096 | 0.81466 | 18.55374 | 5.25495 |
| 10.0 | 1.17038 | 1.06987 | 0.78963 | 18.97890 | 5.37345 |

Table F4: Kinetic data for alkali-catalyzed transesterification of fryer grease using 1.0% KOH, 6:1 alcohol to oil molar ratio at 30 $^{o}$C

| Time [min] | Concentration [dmol/L] | | | | |
|---|---|---|---|---|---|
| | Triglyceride | Diglyceride | Monoglyceride | Methyl ester | Glycerol |
| 0.0 | 6.35917 | 1.73615 | 0.35193 | 2.61426 | 0 |
| 0.5 | 1.74411 | 1.48610 | 2.16502 | 14.73692 | 3.05203 |
| 1.0 | 1.22559 | 1.23876 | 2.24605 | 16.70611 | 3.73686 |
| 1.5 | 0.94376 | 1.13587 | 2.11906 | 18.36419 | 4.24857 |
| 2.0 | 0.89520 | 1.04555 | 1.98682 | 18.72771 | 4.51968 |
| 3.0 | 0.75407 | 0.92613 | 1.81847 | 19.28427 | 4.94859 |
| 4.0 | 0.73752 | 0.88503 | 1.61338 | 19.66680 | 5.21133 |
| 5.0 | 0.62937 | 0.80494 | 1.58176 | 20.19567 | 5.43118 |
| 6.0 | 0.61710 | 0.77247 | 1.50450 | 20.28946 | 5.55320 |
| 7.0 | 0.51826 | 0.72742 | 1.46536 | 20.83013 | 5.73622 |
| 8.0 | 0.47420 | 0.70303 | 1.41198 | 21.09047 | 5.85805 |
| 9.0 | 0.47040 | 0.67539 | 1.36495 | 21.20300 | 5.93652 |
| 10.0 | 0.32775 | 0.63944 | 1.33159 | 21.92778 | 6.14848 |

Table F5: Kinetic data for alkali-catalyzed transesterification of fryer grease using 1.0% KOH, 6:1 alcohol to oil molar ratio at 40 $^{o}$C

| Time [min] | Concentration [dmol/L] | | | | |
|---|---|---|---|---|---|
| | Triglyceride | Diglyceride | Monoglyceride | Methyl ester | Glycerol |
| 0.0 | 6.54311 | 1.62602 | 0.23016 | 2.44238 | 0 |
| 0.5 | 2.11619 | 1.64475 | 1.40358 | 14.21037 | 3.23477 |
| 1.0 | 0.75212 | 0.95298 | 1.85180 | 19.19369 | 4.84239 |
| 1.5 | 0.58773 | 0.82325 | 2.04322 | 19.72592 | 4.94509 |
| 2.0 | 0.50396 | 0.80813 | 2.06751 | 20.84111 | 5.01970 |
| 3.0 | 0.46007 | 0.76363 | 1.99448 | 21.18597 | 5.18111 |
| 4.0 | 0.43843 | 0.72386 | 1.87726 | 21.29726 | 5.35974 |
| 5.0 | 0.41817 | 0.71724 | 1.76017 | 21.37872 | 5.50370 |
| 6.0 | 0.39795 | 0.65396 | 1.65118 | 21.45661 | 5.69620 |
| 7.0 | 0.37767 | 0.62349 | 1.55112 | 21.53432 | 5.84701 |
| 8.0 | 0.35731 | 0.59582 | 1.45950 | 21.61227 | 5.98666 |
| 9.0 | 0.33689 | 0.57078 | 1.37562 | 21.69054 | 6.11599 |
| 10.0 | 0.26139 | 0.53059 | 1.29842 | 21.76912 | 6.30888 |

Table F6: Kinetic data for alkali-catalyzed transesterification of fryer grease using 1.0% KOH, 6:1 alcohol to oil molar ratio at 50 $^{o}$C

| Time [min] | Concentration [dmol/L] | | | | |
|---|---|---|---|---|---|
| | Triglyceride | Diglyceride | Monoglyceride | Methyl ester | Glycerol |
| 0.0 | 6.58752 | 1.62716 | 0.21920 | 2.32056 | 0 |
| 0.5 | 1.51509 | 1.34593 | 1.63248 | 16.35593 | 3.94038 |
| 1.0 | 0.69840 | 1.03046 | 1.92262 | 19.82902 | 4.78241 |
| 1.5 | 0.55291 | 0.80845 | 1.81733 | 20.13295 | 5.25519 |
| 2.0 | 0.53502 | 0.79688 | 1.59696 | 21.06561 | 5.50503 |
| 3.0 | 0.51770 | 0.70212 | 1.15700 | 21.23058 | 6.05706 |
| 4.0 | 0.50407 | 0.66042 | 0.83490 | 21.32534 | 6.43449 |
| 5.0 | 0.50049 | 0.63895 | 0.61992 | 21.41587 | 6.67452 |
| 6.0 | 0.47691 | 0.62517 | 0.47955 | 21.50652 | 6.85224 |
| 7.0 | 0.46329 | 0.61429 | 0.38823 | 21.59758 | 6.96807 |
| 8.0 | 0.44964 | 0.60446 | 0.32893 | 21.68907 | 7.05085 |
| 9.0 | 0.43596 | 0.59498 | 0.29043 | 21.78100 | 7.11251 |
| 10.0 | 0.42225 | 0.58559 | 0.26544 | 21.87337 | 7.16061 |

Table F7: Kinetic data for alkali-catalyzed transesterification of fryer grease using 1.5% KOH, 6:1 alcohol to oil molar ratio at 40 $^{o}$C

| Time [min] | Concentration [dmol/L] | | | | |
|---|---|---|---|---|---|
| | Triglyceride | Diglyceride | Monoglyceride | Methyl ester | Glycerol |
| 0.0 | 6.51370 | 1.64733 | 0.25738 | 2.45279 | 0 |
| 0.5 | 1.54825 | 0.90504 | 1.63896 | 16.59669 | 4.32616 |
| 1.0 | 0.45545 | 0.70566 | 1.78272 | 20.68109 | 5.47458 |
| 1.5 | 0.28644 | 0.59844 | 1.73842 | 21.46381 | 5.79510 |
| 2.0 | 0.15989 | 0.50645 | 1.68047 | 22.10427 | 6.07158 |
| 3.0 | 0.14956 | 0.44677 | 1.56021 | 22.33747 | 6.26186 |
| 4.0 | 0.13508 | 0.42639 | 1.46323 | 22.48203 | 6.39370 |
| 5.0 | 0.12116 | 0.42376 | 1.38404 | 22.61991 | 6.48944 |
| 6.0 | 0.10724 | 0.42069 | 1.32143 | 22.75814 | 6.56905 |
| 7.0 | 0.09328 | 0.41783 | 1.27132 | 22.89727 | 6.63597 |
| 8.0 | 0.07930 | 0.41195 | 1.23214 | 23.03736 | 6.69502 |
| 9.0 | 0.06528 | 0.40289 | 1.20204 | 23.17840 | 6.74820 |
| 10.0 | 0.05123 | 0.39057 | 1.17960 | 23.23090 | 6.79701 |

Table F8: Kinetic data for alkali-catalyzed transesterification of fryer grease using 1.0% KOH, 9:1 alcohol to oil molar ratio at 40 $^{o}$C

| Time [min] | Concentration [dmol/L] | | | | |
|---|---|---|---|---|---|
| | Triglyceride | Diglyceride | Monoglyceride | Methyl ester | Glycerol |
| 0.0 | 5.82502 | 1.55354 | 0.33466 | 2.34687 | 0 |
| 0.5 | 3.86156 | 1.75021 | 0.75642 | 7.28654 | 1.34503 |
| 1.0 | 2.56974 | 1.56925 | 1.00714 | 11.22554 | 2.56709 |
| 1.5 | 1..8098 | 1.31555 | 0.93671 | 14.2015 | 3.65116 |
| 2.0 | 1.61991 | 1.22293 | 0.92197 | 14.89031 | 3.9484 |
| 3.0 | 1.18111 | 1.00961 | 0.76773 | 16.83349 | 4.75477 |
| 4.0 | 1.10749 | 0.96984 | 0.64828 | 17.28054 | 4.98761 |
| 5.0 | 0.81905 | 0.80411 | 0.57128 | 18.65196 | 5.51878 |
| 6.0 | 0.6397 | 0.71107 | 0.53504 | 19.35615 | 5.82742 |
| 7.0 | 0.63717 | 0.69474 | 0.48273 | 19.46091 | 5.89858 |
| 8.0 | 0.63465 | 0.67841 | 0.43041 | 19.56567 | 5.96975 |
| 9.0 | 0.57495 | 0.63817 | 0.41081 | 19.85188 | 6.08929 |
| 10.0 | 0.45501 | 0.57972 | 0.39072 | 20.35672 | 6.28776 |

Table F9: Kinetic data for alkali-catalyzed transesterification of fryer grease using 1.0% KOH, 12:1 alcohol to oil molar ratio at 40 $^{o}$C

| Time [min] | Concentration [dmol/L] | | | | |
|---|---|---|---|---|---|
| | Triglyceride | Diglyceride | Monoglyceride | Methyl ester | Glycerol |
| 0.0 | 5.34775 | 1.43382 | 0.29851 | 2.16820 | 0 |
| 0.5 | 2.77890 | 1.76595 | 1.44286 | 7.62594 | 1.09237 |
| 1.0 | 1.70917 | 1.57889 | 1.85122 | 10.86038 | 1.94080 |
| 1.5 | 1.26051 | 1.38653 | 1.92268 | 12.62220 | 2.51036 |
| 2.0 | 1.06201 | 1.24088 | 1.84898 | 13.74611 | 2.92821 |
| 3.0 | 0.94606 | 1.04203 | 1.55472 | 14.62133 | 3.53728 |
| 4.0 | 0.85144 | 0.91417 | 1.26732 | 15.61550 | 4.04715 |
| 5.0 | 0.76669 | 0.80778 | 1.01367 | 16.29945 | 4.49194 |
| 6.0 | 0.74786 | 0.77770 | 0.82989 | 16.64005 | 4.72464 |
| 7.0 | 0.70690 | 0.69698 | 0.61915 | 17.01606 | 5.05705 |
| 8.0 | 0.65437 | 0.64969 | 0.42911 | 17.67015 | 5.34691 |
| 9.0 | 0.62619 | 0.61390 | 0.34970 | 17.92491 | 5.49028 |
| 10.0 | 0.56288 | 0.57279 | 0.30789 | 18.25050 | 5.63652 |